Coordination Chemistry Reviews
219–221 (2001) 53–80

COORDINATION
CHEMISTRY
REVIEWS

www.elsevier.com/locate/ccr

Electron-transfer induced isomerizations of coordination compounds

Armando J.L. Pombeiro *, M. Fátima C. Guedes da Silva, M. Amélia N.D.A. Lemos

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais,
1049-001 Lisbon, Portugal

Received 4 August 2000; received in revised form 7 November 2000; accepted 29 November 2000

Dedicated to Professor A.B.P. Lever on the occasion of his 65th birthday

Contents

Abstract

Geometrical isomerization processes induced electrochemically are reviewed for octahedral-type complexes, in particular with π-electron acceptor ligands, with focus on those whose mechanisms have been established in terms of square ECEC-type schemes and electron-transfer chain catalysis. Rationalizations based on the isomeric redox potential differentiation are also presented. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molecular electrochemistry; Redox processes; Electron-transfer; Isomerization; Mechanisms; Octahedral complexes

---

* Corresponding author. Tel.: +351-218-419237; fax: +351-218-454455.
E-mail address: pombeiro@ist.utl.pt (A.J.L. Pombeiro).

PII: S0010-8545(01)00299-5

1. Introduction

Electron-transfer (ET)-induced structural changes of coordination compounds constitute a matter of growing interest and electrochemistry provides convenient tools for the investigation of the subject [1–9], although they can also result [8] from chemical redox reactions. Examples include ET-promoted changes of hapticity either in poly-hapto polyolefinic and aromatic ligands [7,10] (with possible involvement of ring slippage and other rearrangements) or in low-hapto ligands such as carbonyl [11a], dithiocarbamate [11b,c] and others [11d–g], conformational changes in macrocyclic complexes [12] and other chelates [13], linkage isomerizations in complexes with ambident ligands [11d–g,14], alkyne–vinylidene isomeric interconversion [15] and geometrical isomerizations for particular coordination numbers [1,6,16]. In particular, for the mostly studied octahedral-type complexes, geometrical isomerizations can readily result from ET and the dependence of the relative stability, and redox behavior of the geometrical isomers on the electronic configuration of the metal, although known for a long time [6], is still a matter of debate in a number of cases that can involve differing semiempirical predictions of the redox potentials [17], theoretical calculations [18–20] and experimental observations [21–25].

The present review concerns the *cis*/*trans* and *fac*/*mer* octahedral-type isomeric redox systems and provides attempts for rationalization, with emphasis on those which have been object of a detailed mechanistic study, in particular, involving complexes with π-electron acceptor ligands (e.g. carbonyl, isocyanides or nitriles), such as those studied in our laboratory, and related systems.

The description of the systems is presented according to the mechanisms involved, in a systematic way, starting with the single square-type ECEC scheme (E — electron transfer, C — chemical process) followed by the more complex extended (ladder) square and electron-transfer chain (ETC) catalytic types.

Within each type of mechanism, the relevant features are provided for a better understanding of the presentation, which starts with the studies, if available, on mononuclear carbonyl systems (complexes with carbonyl ligands have usually been the most studied).

Thermodynamic and kinetic gains towards the electrochemically promoted isomerization result from the ET and are dependent on structural, electronic and steric factors. Although their role has not yet been fully established, conceivable interpretations are included.

The IUPAC convention that oxidation processes have positive current has been adopted in this the review, and the potentials are quoted relative to the saturated calomel electrode (SCE). The use of the reversible ferricinium/ferrocene redox couple has also been frequently encountered in the literature, but the potentials can easily be interconverted in the two scales by considering that, for this redox couple, $E° = 0.53$ or 0.55 V vs. SCE (in 0.2 M $[NBu_4][BF_4]/CH_2Cl_2$ or THF, respectively).

2. *Cis/trans* isomerization

2.1. Square (ECEC) mechanism

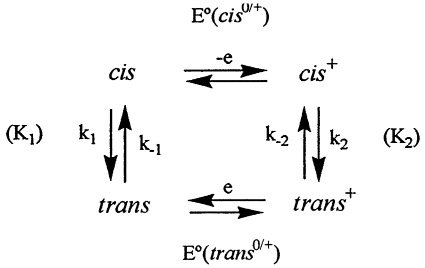
For a system in which the 18-electron configuration is more stable in the *cis* form while the singly oxidized 17-electron state is more stable in the *trans* form, the conversion of the former into the latter can occur upon its oxidation ($cis^{+} \rightarrow trans^{+}$) whereas the reverse isomerization can result upon reduction of $trans^{+}$, i.e. $trans \rightarrow cis$. These redox-induced isomerizations can be monitored conveniently by voltammetric techniques and follow a square (ECEC) or four-component mechanism (Scheme 1) involving two EC sequences in which $E°(cis^{0/+})$ and $E°(trans^{0/+})$ are the standard redox potentials for the $cis^{0/+}$ and $trans^{0/+}$ couples, and K_1 and K_2 are the isomerization equilibrium constants for the reduced and oxidized forms, respectively, i.e. $K_1 = [trans]/[cis] = k_1/k_{-1}$ and $K_2 = [trans^{+}]/[cis^{+}] = k_2/k_{-2}$ (k_1 and k_2 are the corresponding forward rate constants, whereas k_{-1} and k_{-2} are the backward rate constants, respectively).

The isomerization equilibrium constants and the redox potentials are related by Eq. (1) derived from the well-known relationship between the standard Gibbs free energy change ($\Delta G°$) and the equilibrium constant (K) or the standard potential, i.e. $\Delta G° = -\mathrm{R}T \ln K = -nFE°$, and by taking into consideration that $\Delta G° = 0$ for the thermochemical cycle.

$$\frac{K_2}{K_1} = \exp\left[\frac{F}{\mathrm{R}T}\{E°(cis^{0/+}) - E°(trans^{0/+})\}\right] \tag{1}$$

Hence, for $E°(cis^{0/+}) > E°(trans^{0/+})$, a common situation in di- and tri-carbonyl complexes (see below), one concludes that $K_2 > K_1$, i.e. $[trans^{+}]/[cis^{+}] > [trans]/[cis]$; therefore, the oxidation results in a shift of the isomeric equilibrium towards the *trans* geometry. The ratio K_2/K_1 represents the equilibrium constant [K, Eq. (2)] for the cross redox reaction, Eq. (3), whose equilibrium position should thus lie to the right, i.e. towards the most stable *cis* and $trans^{+}$ isomers.

$$K = \frac{[trans^{+}][cis]}{[cis^{+}][trans]} = \frac{K_2}{K_1} \tag{2}$$



Scheme 1. Square scheme for a redox-induced *cis/trans* isomerization.

$$cis^{+} + trans \rightleftarrows cis + trans^{+} \tag{3}$$

However, one should stress the determining role of the relative values of the redox potentials of the isomers, since the above conclusions are only valid when $E°(cis^{0/+}) > E°(trans^{0/+})$. In fact, if $E°(cis^{0/+}) = E°(trans^{0/+})$ there will be no shift of the isomeric equilibrium upon oxidation ($K_1 = K_2$), whereas when $E°(cis^{0/+}) < E°(trans^{0/+})$ (a situation that will be treated separately, Section 2.3) the isomeric equilibrium will shift towards the *cis* geometry (rather than the *trans*) as a result of oxidation ($K_2 < K_1$).

Nevertheless, the most commonly studied situation is that of $E°(cis^{0/+}) > E°(trans^{0/+})$, being typified by 18-electron octahedral-type dicarbonyl complexes (see below) of the general type $[ML_2L'_4]$ ($L = CO$). It can be interpreted by considering a semi-empirical rationalization [17] for the differences of the oxidation potentials for isomeric pairs, on the basis of the additive effects of the ligands upon the energetics of the metal d_π orbitals, as given by an empirically obtained parameter (a "bonding term") which constitutes a measure of the relative ability of each ligand to stabilize a given metal d_π orbital (that is dependent on the π-backbonding capability of the metal center). This term is proportional to the number (x) of ligands L that interact with the d_π orbital that comprises the HOMO of the complex.

The above situation can be represented by Fig. 1, on the basis of the expected ligand field splitting for the metal-centered filled d_π orbitals, assuming that L is a better π-electron acceptor than L′. For a metal d^6 complex, the HOMO is derived from the d_π orbital having the fewest interactions (x) with ligand L.

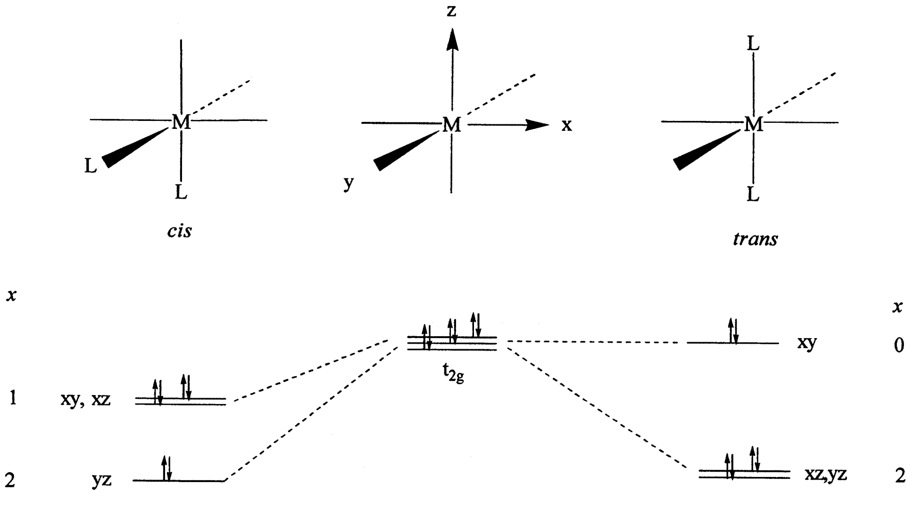


Fig. 1. d_π orbital level splitting for *cis* and *trans* isomers of $[ML_2L'_4]$ where L is a better π-electron acceptor than L′ (x is the number of L ligands that can interact with a given metal d_π orbital) (adapted from Ref. [17]). The filling of orbitals corresponds to d^6 metal complexes.

Hence, for the isomeric pair [$ML_2L'_4$] with a metal d^6, the higher energy level of the HOMO in the *trans* relative to the *cis* isomer (d_{xy} vs. d_{xy} or d_{xz}, respectively) accounts for the lower oxidation potential for the former; moreover, oxidation favors the stabilization of the former geometry *(trans*$^+$) (the electron is removed from a more destabilized orbital) in relation to the latter. Similar arguments apply to the pair of *meridional* and *facial* isomers, respectively, for the [$ML_3L'_3$] systems, which will be discussed in Section 3.

The square scheme is well known, being introduced [26] in a process with protonation coupled to ET, and has been applied to a number of situations [27,28] and, in particularly favorable ones, it is susceptible to a "complete" analysis (allowing the determination of the above-mentioned equilibrium and rate constants [27]) by electrochemical methods.

The cyclic voltammograms can also be simulated, and typical situations are illustrated in Fig. 2 which shows the promotion of the extent of the anodically induced isomerization on enhancing its rate [increase of k_2/k_1, i.e. fastening the isomerization kinetics for the oxidized complex, from (a) to (c) or (b) to (d)] and on slowing down the scan rate [from (a) to (b) or (c) to (d)].

Typical examples concerning geometrical isomerization coupled to ET are provided by the octahedral-type dicarbonyl–phosphine complexes [$M(CO)_2(LL)_2$]$^{0/+}$ {M = Cr [29–31], Mo or W [25,30,32]; LL = $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH{=}CHPPh_2$ (dppen) or (only for Cr) $(MeO)_2PCH_2CH_2P(OMe)_2$ (pompom). M = Re [33], LL = dppm or *o*-$Ph_2PC_6H_4PPh_2$ (dpbz)}, [$MX(CO)_2(L_2L')$] [M = Mn or Re, X = Cl or Br, $L_2L' = \eta^3$-$Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$ (triphos)] [34], and by the mono-carbonyl compounds [$ReBr(CO)(LL)_2$] (LL = dppe, dppm or dpbz) [33], mainly studied by Bond's group [6]. They can exist in two isomeric forms, *cis* and *trans*, which are oxidized at well-separated potentials (see Fig. 1), the one for the redox couple *cis*$^{0/+}$ being higher than that for *trans*$^{0/+}$ [by ca. 0.35 V (M = Cr) or ca. 0.14 V (M = Mo or W) for the dppe complexes].

The systems were investigated by a variety of electrochemical methods, in some cases associated with IR, ^{31}P or EPR spectroscopies and electrospray mass spectrometry [29–31,33,34], as well as by theoretical studies [31]. Those methods include voltammetric techniques, such as conventional cyclic voltammetry [25], thin-layer cyclic voltammetry [27], diffusion linear potential sweep voltammetry [27], steady-state microelectrode voltammetry [29,33], convolution and deconvolution potential sweep voltammetry [32] and rotating-disk voltammetry [29], as well as polarography [25] and controlled potential electrolysis; the theoretical analyses of the data indicate a number of interesting thermodynamic and kinetic features, such as:

1. Isomerization occurs in both the oxidized 17-electron and the starting 18-electron complexes, but the isomeric equilibrium is shifted more towards the more stable form in the former case, i.e. *trans*$^+$ (in the equilibrium *cis*$^+$ ⇄ *trans*$^+$) in comparison with *cis* (in the *cis* ⇄ *trans* equilibrium). In other words, $K_2 = [trans^+]/[cis^+] > K_1^{-1} = [cis]/[trans]$ (e.g. K_2/K_1^{-1} ca. 10^5, 66 or 12, in the above dicarbonyl phosphinic complexes, for M = Cr [29], Mo or W [27], LL = dppe). Hence, there is a clear thermodynamic gain towards the *trans* isomer upon oxidation.

2. The isomerization is faster in both directions for the 17-electron system ($cis^+ \rightleftarrows trans^+$) than for the 18-electron one ($cis \rightleftarrows trans$). Hence the rate towards the more stable oxidized form ($trans^+$) is greater than that towards the more stable neutral one (cis), i.e. $k_2(cis^+ \rightarrow trans^+)/k_{-1}(trans \rightarrow cis)$ ca. 6 (M = Cr, LL = dppm [30], ca. 10^3 [27,30] (M = Mo, LL = dppe) and ca. 10^2 [27,30] (M = W, LL = dppe). The slow rate of isomerization at the 18-electron level ($trans \rightarrow cis$) is indicated by the relatively low value of the corresponding rate constant (k_{-1} ca. 0.05 s^{-1} at ca. 20°C for *trans*-[$Mo(CO)_2(dppe)_2$] [30,32]. Therefore, there is a clear kinetic gain upon oxidation.

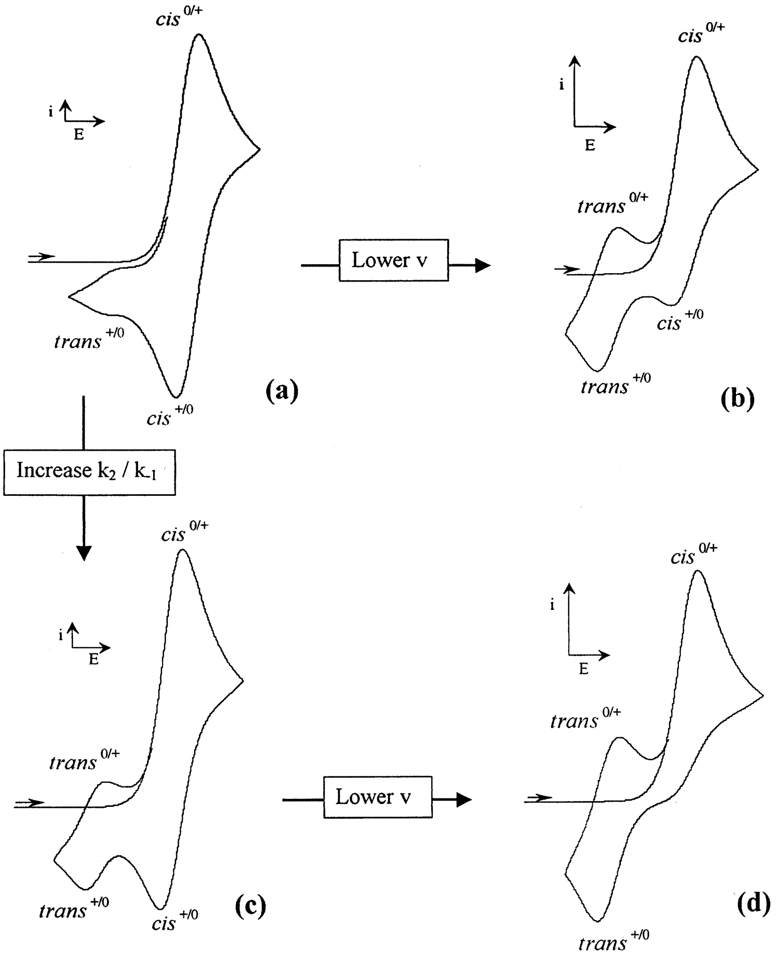


Fig. 2. Simulated cyclic voltammograms for redox processes following the square scheme (Scheme 1) (anodically induced *cis*-to-*trans* isomerization) (this work). Units 0.1 V (E) for the potential, arbitrary unit (i) for the current. ($E°(cis^{0/+}) - E°(trans^{0/+}) = 0.2$ V. $K_2/K_1 = 5000$, $K_1 = 0.1$, $k_1 = 0.01$ s^{-1}. (a) $k_2 = 5$ s^{-1}, $v = 10$ V s^{-1}; (b) $k_2 = 5$ s^{-1}, $v = 0.8$ V s^{-1}; (c) $k_2 = 20$ s^{-1} $v = 10$ V s^{-1}; and (d) $k_2 = 20$ s^{-1}, $v = 0.8$ V s^{-1}.

3. The isomerizations occur with negative entropies of activation ($\Delta S^{\neq}$), at rates which are essentially independent of the concentrations of phosphine (LL) and CO, and as well as of the solvent, thus suggesting that they proceed via a twist mechanism rather than through a dissociative (metal–ligand bond breaking) process [27,30]. Nevertheless, for the $[Cr(CO)_2(dppe)_2]^{0/+}$ system, a more complex situation is observed [29], particularly a recognized solvent dependence (although only to a moderate extent) of the isomeric distribution of the non-oxidized *cis* and *trans* isomers, which is affected by the presence of *trans*$^+$ (formed by aerial oxidation of the readily oxidizable *trans* complex, $E_{\frac{1}{2}}^{ox} = -0.52$ V vs. SCE [29]).

Other complications have been observed in some cases, namely involving side reactions competing with the ET-induced isomerization and evidence has been presented [34] for the occurrence of disproportionation of the Re(II) complex *cis,mer*-$[ReBr(CO)_2(L_2L')]^+$ (obtained by single-electron oxidation of the parent neutral compound) to the corresponding Re(I) and Re(III) species *cis,mer*-$[ReBr(CO)_2(L_2L')]$ and $[ReBr(CO)_2(L_2L')]^{2+}$, respectively, in competition with the isomerization to *trans,mer*-$[ReBr(CO)_2(L_2L')]^+$.

Extended Hückel calculations were performed [31] for the model complexes *cis*- and *trans*-$[Cr(CO)_2L_4]$ [L = PH_3 or $P(OH)_3$], *cis*- and *trans*-$[Cr(CO)_4L_2]$, as well as for *mer* and *fac*-$[Cr(CO)_3L_3]$, and were consistent with the theoretical studies [20] of related Mo compounds. The composition and the energy of the HOMO were calculated for all the isomers and the predicted trend in the redox potentials or in the energies of the ET reactions were in accord with the experimental data, but the prediction of the relative stability of the isomers was not reliable, being strongly dependent on the bond lengths used in the calculations [31].

The mixed carbonyl–isocyanide complexes $[Mo(CO)_2(CNR)_2(PR'_3)_2]$ (R, R′ = alkyl or aryl), which can exist either as a single isomer (usually R = alkyl) or as a mixture of isomers (R = aryl) undergo a single-electron reversible oxidation followed by a rapid isomerization to the corresponding all-*trans* cations (identified by IR and X-band EPR spectroscopies) which in turn rapidly isomerize back upon reduction normally to regenerate the isomer of the equilibrium mixture of isomers present in the starting complexes [35]. The reversibility of the isomeric interconversion and the similarity of the electrochemical behavior in various solvents support the involvement of a non-dissociative mechanism, which is suggested [35] to occur via intramolecular sequential trigonal twists.

The homogeneous chemical rate constants for the *cis–trans* isomerizations have been estimated by cyclic voltammetry and their values (in the 0.20–1.38 s^{-1} range [35]) are somewhat lower than those measured (20–30 s^{-1} [30]) for the related chelating phosphine complexes $[Mo(CO)_2(LL)_2]$ mentioned above. However, as in the latter complexes, the isomerization of the cationic species (*cis*$^+ \rightarrow$ *trans*$^+$) is faster [35] than that of the neutral ones (*trans* → *cis*), i.e. $k_2 > k_{-1}$ (Scheme 1).

From the separation between $E°(cis^{0/+})$ and $E°(trans^{0/+})$, the equilibrium constant for the redox cross-reaction 3 was evaluated (average 5.4×10^3), showing that the equilibrium lies far to the side of the most stable *trans*$^+$ and *cis* isomers [35].

In contrast with the above cases in which the *cis* isomers are oxidized at a more anodic potential than the *trans* ones, systems with identical redox potentials, $E°(cis^{0/+}) = E°(trans^{0/+})$ or even with the inversion of the order of their values, $E°(cis^{0/+}) < E°(trans^{0/+})$, are also known to exist. The latter will be considered separately (Section 2.3, ETC catalysis). Now let us consider the former one which is expected for complexes of the general type $[ML_4L'_2]$ (L = better π-electron acceptor than L′). In fact, simplified d_π orbital-level splitting for both isomers, depicted in Fig. 3, predicts identical oxidation potential values for d^6 metal complex isomers, in view of the similarity of the energies of the HOMOs (d_{xz} for *cis*, and d_{xz} or d_{yz} for *trans*). In accord, the *cis* and *trans* isomers of the tetracarbonyl complexes $[Cr(CO)_4L'_2]$ [L′ = $P(OMe)_3$ or $P(OEt)_3$] present similar oxidation potentials [36]. Nevertheless, the oxidation of the *cis* isomers results in a fast $cis^+ \rightarrow trans^+$ isomerization and the *trans*-$[Cr(CO)_4L'_2]^+$ products have been identified by IR spectroscopy of the electrolyzed solutions [36].

Similarly, in the systems $[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) in which the phosphine ligand is believed to behave as a stronger π-electron acceptor than N_2, the *cis* and the corresponding *trans* isomers oxidize at a common potential [e.g. $E^{ox}_{1/2} = -0.83$ V (M = W) vs. the ferricinium/ferrocene couple], although for the former isomer the oxidized form readily loses N_2. However, no redox-induced isomerization has been detected in this system [22,23].

The above systems involve 18-/17-electron complexes with d^6 metals at the lower redox level, but a study on a 16-/15-electron system was also reported [37]. It concerns the thiolateisocyanide 16-electron Mo(II), d^4, compounds *cis*-$[Mo(tipt)_2(CNR)_4]$ (tipt = $SC_6H_2{}^iPr_3$-2,4,6; R = Me or ^{t}Bu) which undergo an anodically induced *cis*- to *trans*- isomerization (electrochemical study performed at −50°C) [37].

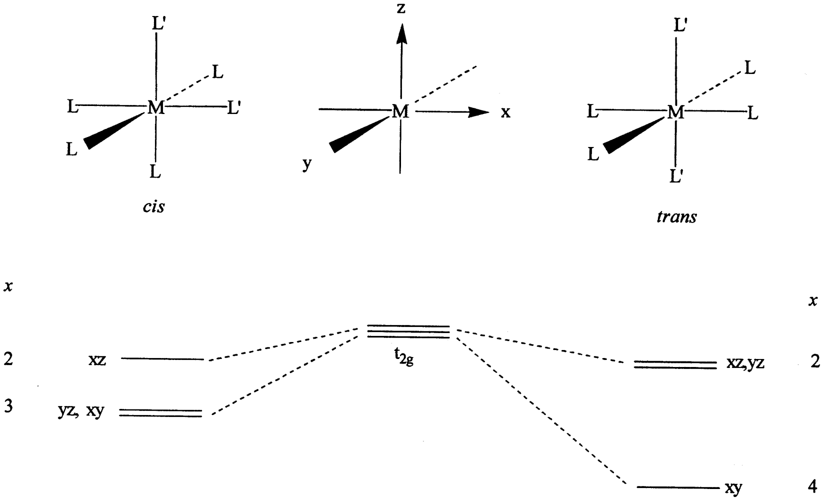


Fig. 3. d_π orbital level splitting for the *cis* and *trans* isomers of $[ML_4L'_2]$ where L is a better π-electron acceptor than L′ (*x* is the number of L ligands that can interact with a given metal d_π orbital) (this work).

The equilibrium *cis* ⇄ *trans* lies very much in favor of the *cis* isomer ($K_1 = 1.7 \times 10^{-4}$) (Scheme 1), but single-electron oxidation promotes the isomerization mainly on thermodynamic grounds ($K_2 = 2$, i.e. a gain of ca. 10^4), although the kinetics are also accelerated, i.e. the conversion into the more stable species is faster at the cationic 15-electron level [$k_2(cis^+ \rightarrow trans^+) = 5\ s^{-1}$] than at the neutral 16-electron level [$k_{-1}(trans \rightarrow cis) = 1\ s^{-1}$] [37].

A cyclic voltammogram of *cis*-[Mo(tipt)$_2$(CN^{t}Bu)$_4$] is shown in Fig. 4(a) and the formation of the *trans*$^+$ isomer upon oxidation of the *cis* is clearly recognized by the detection, on scan reversal, of the cathodic wave of *trans*$^+$. The simulated voltammogram, in perfect agreement with the experimental one, is depicted in Fig. 4(b) [37].

The oxidation potential of the *cis* isomer, $E°(cis^{0/+}) = -0.09$ V vs. SCE, is higher than that of the *trans* one, $E°(trans^{0/+}) = -0.27$ V vs. SCE [37], and this can be accounted for by the simplified d_π orbital-level splitting depicted in Fig. 3 for [$ML_4L'_2$] complexes (L = better π-electron acceptor than L′). In the present case (M = Mo, L = CNR, L′ = tipt), a d^4 metal complex, the HOMO of the *cis* isomer is stabilized relatively to that of the *trans* one by the interaction of a higher number (3 instead of 2) of π-acceptor CNR ligands with the corresponding d_π metal orbital.

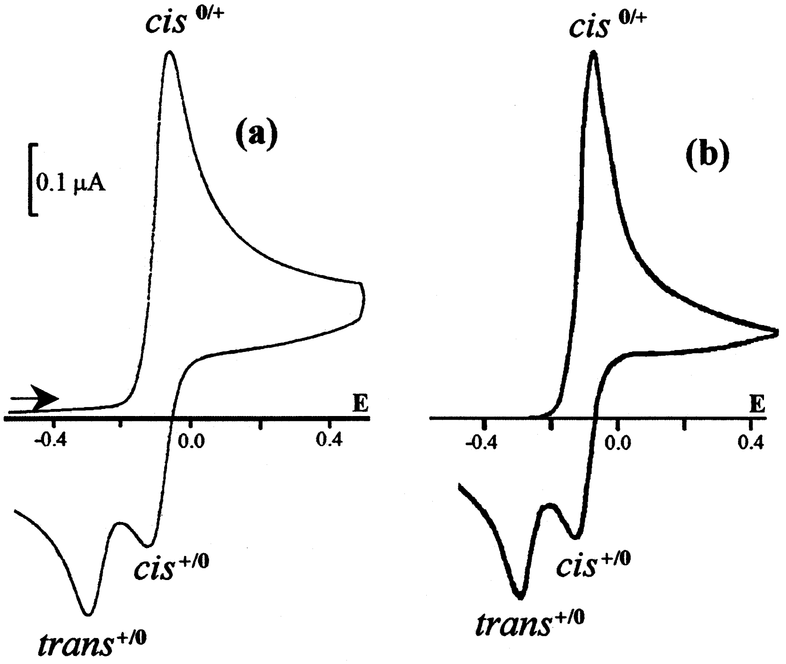


Fig. 4. Experimental (a) and simulated (b) (according to the mechanism in Scheme 1 where $k_1 = 5$, $k_{-1} = 2.5$, $k_{-2} = 1$ and $k_2 = 0$ s^{-1}) cyclic voltammograms at 0.8 V s^{-1} of a solution of *cis*-[Mo(tipt)$_2$(CN^{t}Bu)$_4$] (1.13 mM) in CH$_2$Cl$_2$ with 0.2 M [Bu$_4$N][BF$_4$], at −50°C and at a Pt disc (0.5 mm diameter) electrode. Potential in volts vs. SCE [37].

An analysis of the electronic vs. steric factors controlling the geometrical preference of the metal oxidation state in hexacoordinate complexes has been presented in a few cases [36,38–40]. Hence, oxidation of 18-electron phosphinic complexes with two strong electron-acceptor ligands (L) usually leads to the stabilization of the *trans* relative to the *cis* isomer (as discussed above), or of the *mer* relative to the *fac* (see below), thus favoring the *trans* arrangement of the L ligands. In these 17-electron systems both electronic and steric factors favor the *trans* (or *mer*) form, in contrast with the 18-electron systems, when competing influences of such factors can occur. Thus, for a variety of 18-electron Group 6 tri- or tetra-carbonyl complexes of type $[M(CO)_3L_3]$ (M = Cr, Mo or W; L = organophosphine or phosphite ligand) or $[M(CO)_4L_2]$, although the *cis* or *fac* arrangement are favored on electronic grounds, the corresponding *trans* or *mer* isomers can become the thermodynamically stable species as a result of steric effects in the case of bulky L ligands [36]. Moreover, unusual alterations in the common relative stabilities of fac^+ and mer^+ can also occur in sterically constrained systems [38] which will be discussed below.

The combination of electronic and steric factors on the control of the geometry has also been discussed [39] for the dithiocarbonate or dithiocarbamate complexes of ruthenium(II,III) $[RuX_2(PPh_3)_2]^{0,+}$ [X = $ROCS_2$ (R = alkyl) [39b] or S_2CNEt_2 [39a], respectively] and osmium(II,III) analogues [40]. The stable species are the neutral *cis* and the oxidized $trans^+$, as in the above examples, and the oxidation of the former induces isomerization of the latter. For the neutral M(II, d^6) complexes, the electronic factors dominate and the M–P nd_π–$3d_\pi$ back-bonding from the metal to the phosphine ligands is favored by the *cis* geometry which thus is more stable than the *trans* one, in spite of the steric disadvantage of the former. However, in the oxidized cationic M(III, d^5) complexes, with the metal presenting a weak π-backbonding capacity, the effect of the steric repulsion between the two PPh_3 ligands overcomes the electronic effect and the *trans* geometry becomes the most stable one [39a].

The rates of isomerization (both $cis^+ \rightarrow trans^+$ and $trans \rightarrow cis$) are slower (by at least one order of magnitude) for the Os, relative to the Ru complexes (which present more anodic oxidation potentials than the analogous Os compounds), allowing the isolation at low temperature of *trans*-$[Os(S_2CNEt)_2(PPh_3)_2]$, although in the case of the Ru complexes the less stable species (cis^+ and *trans*) have been only detected by cyclic voltammetry at low temperature.

A dependence of a diastereomeric preference on the metal oxidation state was recognized [41] for the $[Ru(acac)_2(LL')]^{0/+}$ (acac = acetylacetonate, LL′ = chelating olefinic N- and O-donor ligand) couple in which the single-electron oxidation of Ru(II) to Ru(III) promotes the conversion of one diastereomer to the other (their redox potentials differ by ca. 0.10 V) conceivably via a square-type process whose kinetics, however, were not investigated in detail.

An unusual cathodically induced *trans*-to-*cis* isomerization has been reported [42] for a 16-/17-electron system comprising a cyclam Mn(III, d^4) complex without π-acceptor ligands, *trans*-$[MnCl_2(cyclam)]Cl$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) (the reaction does not occur for the analogous iron or cobalt complexes).

The Mn(III) complex, in dimethylsulfoxide, upon single-electron reduction, forms the neutral *cis* isomer (isomerization rate constant of 5.8 s^{-1}) which, by oxidation, undergoes the usual *cis*-to-*trans* isomerization to give the above parent cationic complex (at a lower rate of isomerization, 0.1 s^{-1}) [42]. The kinetics were studied by simulation of double-step chronoamperometry and cyclic voltammetry. Another example of cathodic *trans* → *cis* isomerization is provided by some Fe(III) complexes of tridentate heteroscorpionate ligands, $[Fe(\eta^3\text{-}L)_2]^+$ [L = (2-hydroxyphenyl)bis(pyrazolyl)methane and derivatives], which cathodically isomerize to the *cis* forms, the latter regenerating the former isomers on oxidation [43]. The systems were studied by cyclic voltammetry (the kinetics were established by digital simulation) and resonance Raman spectroscopy.

Anodically induced *cis* → *trans* isomerization can also occur at a metal fragment in a *binuclear complex* and the process may be triggered by an intramolecular ET between the two metals.

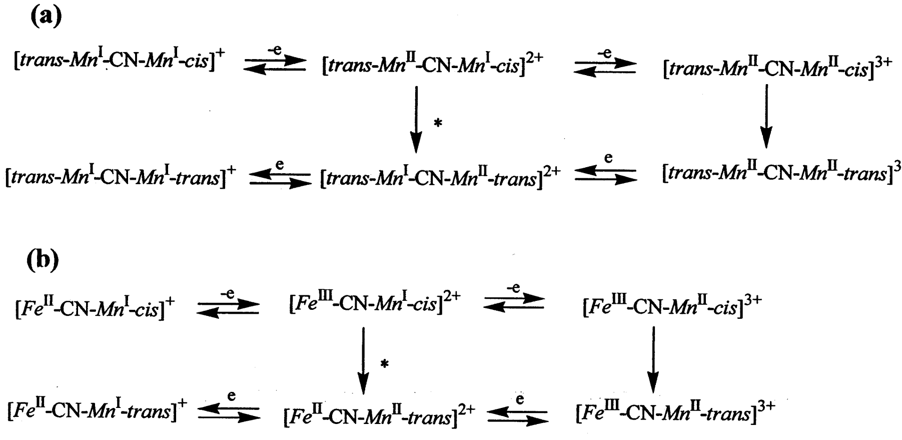
Hence, if in a binuclear complex with a bridging ligand, $\overset{\frown}{M_1 M_2}$, the oxidation potential of the M_1 fragment is lower than that of M_2, and if the latter one has another isomeric form, M_2', with an oxidation potential lower than that of M_1, the isomerization can occur according to reaction sequence (4), provided the bridge allows an ET between the two metals [44] (the isomerization induced by intramolecular ET is denoted by an asterisk):

$$\overset{\frown}{M_1 M_2} \overset{-e}{\rightleftharpoons} \overset{\frown}{M_1^{ox} M_2} \xrightarrow{*} \overset{\frown}{M_1 M_2'^{\,ox}} \qquad (4)$$

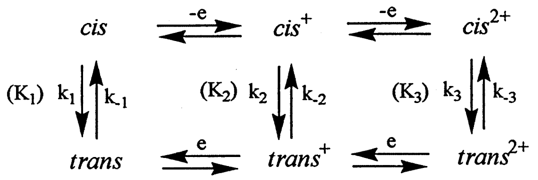
This situation has been encountered for some members of the series of cyanide-bridged cationic carbonyl complexes of the type $[L(LL)(CO)_2Mn\text{–}CN\text{–}Mn(CO)_2(LL)'L']^+$ [L, L′ = $P(OPh)_3$ or PEt_3; LL, (LL)′ = dppm or dppe] [45,46] or $[(\eta^5\text{-}C_5H_5)(LL)Fe\text{–}CN\text{–}Mn(CO)_2(LL)'L]$ [44], as shown by cyclic voltammetry complemented with chemical oxidation and IR spectroscopy, although no kinetic measurements have been reported.

The manganese fragments present two carbonyl ligands which can be either in *trans* or in *cis* position. The oxidation of the *trans*-dicarbonyl fragment occurs at a lower potential than that of the *cis* and with retention of the stereochemistry, but the oxidation of a *cis*-dicarbonyl fragment induces isomerization to the *trans* form as observed in the mononuclear species discussed above. However, in these binuclear complexes, oxidation of a *cis* site can occur upon intramolecular ET to the other metal fragment, under the conditions indicated above, as shown by Scheme 2(a) [45] for the di-manganese complexes, and by Scheme 2(b) [44] for the iron–manganese compounds, in which M denotes the metal fragment; the steps involving *cis* → *trans* isomerization induced by intramolecular ET are marked by an asterisk.

This intramolecular oxidative isomerization process occurs as a result of the intermetallic interaction via the cyanide bridge, which, in turn, increases as the redox potentials of the two metal centers come closer to each other, the process then becoming faster [44,45].



Scheme 2. Oxidative isomerizations triggered by an intramolecular ET [44,45].



Scheme 3. Double square scheme for redox induced *cis*/*trans* isomerization.

2.2. Extended square mechanisms

The activation of a complex towards redox-induced geometrical isomerization can require, in some cases, the *transfer of more than one electron* in order to occur at an appreciable extent, and a system is known [47] which has been studied in great detail from both a kinetic and a thermodynamic point of view and has been shown to involve a mechanism within the general double square type shown in Scheme 3. It comprises the 18-electron *cis*- and *trans*-nitrile complexes $[ReCl(NCR)(dppe)_2]$ ($R = C_6H_4Me\text{-}4$) which have been investigated by cyclic voltammetry, digital simulation and controlled-potential electrolysis (with product isolation).

The *cis* isomer is oxidized via two successive single-ETs, at potentials $E°(cis^{0/+}) = -0.13$ V and $E°(cis^{+/2+}) = 0.70$ V vs. SCE, that are higher than the corresponding ones, $E°(trans^{0/+}) = -0.31$ V and $E°(trans^{+/2+}) = 0.67$ V vs. SCE, for the *trans* isomer. The cis^{+} radical cation is stable within the time scale of preparative electrolysis and can be reduced back to the parent *cis* complex. However, the 16-electron cis^{2+} complex undergoes a ready isomerization to the $trans^{2+}$ isomer, which occurs during the time scale of the cyclic voltammetry [47]. The reversibility of this isomerization at the level of dications, i.e. $cis^{2+} \rightleftarrows trans^{2+}$ (K_3 in Scheme 3) was recognized and the values of equilibrium and isomerization rate constants for this and the $cis^{+} \rightleftarrows trans^{+}$ (K_2) and $cis \rightleftarrows trans$ (K_1) processes were estimated: $K_3 = k_3/k_{-3} = 5.6/1 = 5.6$, $K_2 = 1.5$ (with rate constants k_2 and k_{-2} smaller than 10^{-4} s^{-1}) and $K_1 = 6.9 \times 10^{-4}$ [47].

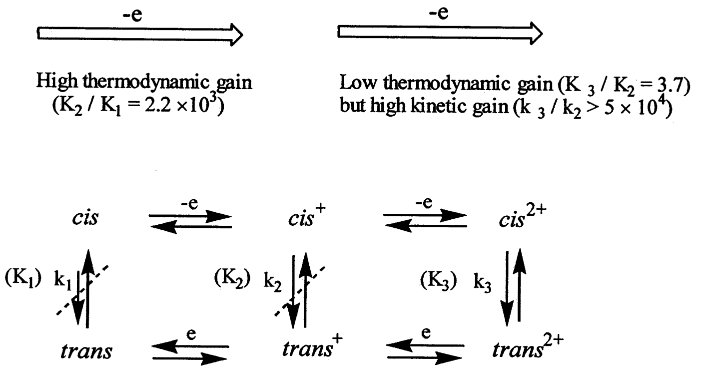
Hence, the *cis* isomer is thermodynamically more stable than the *trans* isomer ($K_1 \ll 1$), and although a single-electron oxidation of the former results in a high gain of the relative thermodynamic stability of the *trans* vs. the *cis* isomer ($K_2/K_1 = 2.2 \times 10^3$), kinetic factors (low rate constant k_2) do not allow the *cis*-to-*trans* isomerization to occur significantly in the time scale of the experiments. Hence, a second oxidation step is required to induce such an isomerization, which then occurs readily for the 16-electron *cis*$^{2+}$ species as a result of the high kinetic gain ($k_3/k_2 > 5 \times 10^4$) in spite of the concomitant modest thermodynamic one ($K_3/K_2 = 3.7$) [47].

In addition, the reverse isomerization (*trans*$^{2+} \rightarrow$ *cis*$^{2+}$), although endergonic, also occurs in electrochemical conditions in accord with the shift of the K_3 equilibrium towards the *cis*$^{2+}$ isomer by its cathodic reduction upon scan reversal [47].

Therefore, in the particular case under study, the double square scheme (Scheme 3) assumes the form of Scheme 4 in which neither the *trans*/*cis* nor the *cis*$^+$/*trans*$^+$ isomerization (i.e. at the 18- or 17-electron level, respectively) occurs (in the time scale of the electrochemical experiment) for kinetic reasons rather than for thermodynamic ones.

Typical cyclic voltammograms are presented in Fig. 5 in which the anodic generation of the *trans*$^{2+}$ isomer is clearly detected by its cathodic waves, upon scan reversal. Holding the potential at the plateau of the second anodic wave (oxidation of *cis*$^+$) before reversing the scan of the potential results in an increase of the amount of the *trans*$^{2+}$ (and therefore also of its derived *trans*$^+$ on reduction), as shown in Fig. 5(b).

The significance of this and other systems, following double square redox process, in terms of developing a "molecular hysteresis" behavior was discussed [14c,14d,48]. In particular the *cis* and the *trans*$^{2+}$ complexes (the more stable 18-



Scheme 4. Thermodynamic and kinetic gains for isomerization induced by sequential ETs in $[ReCl(NCC_6H_4Me\text{-}4)(dppe)_2]$ [47].

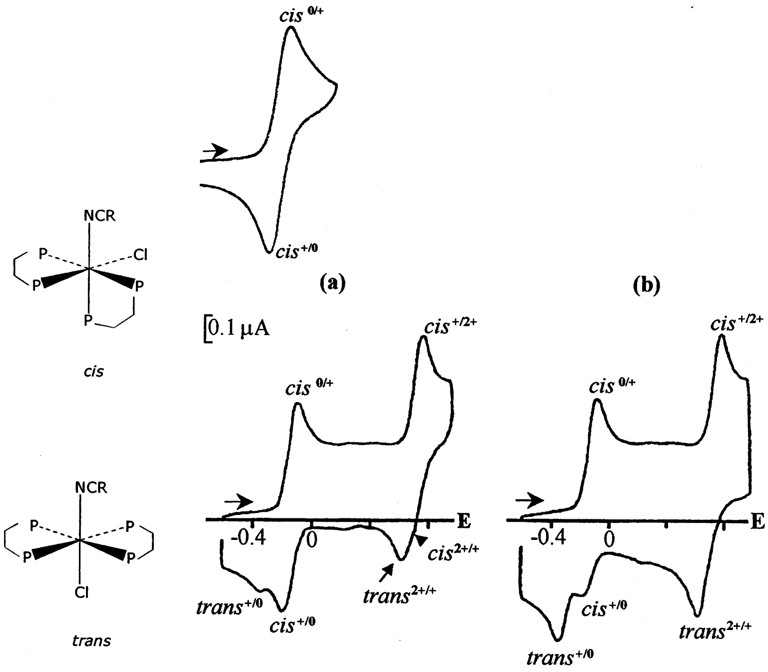
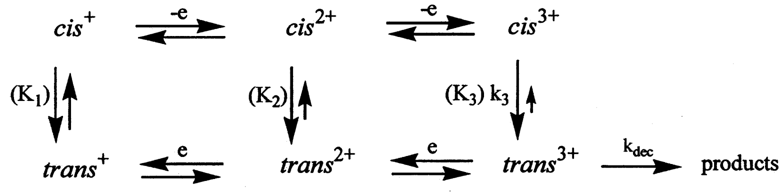


Fig. 5. Cyclic voltammograms of *cis*-[ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$] (0.96 mM) in THF with 0.2 M [NBu$_4$][BF$_4$], at 0°C and at a Pt disc electrode (0.5 mm diameter) at a scan rate of 0.8 V s^{-1}. In (b) the potential was clamped for 10 s at the plateau of the *cis*$^+$ oxidation. In the upper voltammogram the scan was reversed after the first oxidation wave. Potential in volts vs. SCE [47].

and 16-electron forms, respectively) would represent, in a bistable system, the stable states, that can be interconverted by a trigger signal (overall two-electron oxidation or reduction).

A systematic and detailed study of the thermodynamic and kinetic effects of the R group of the nitrile (NCR) ligand was reported [48] for the series of dinitrile complexes *cis*- and *trans*-[Re(NCR)$_2$(dppe)$_2$][BF$_4$] [R = alkyl or aryl, i.e. C$_6$H$_4$NEt$_2$-4, C$_6$H$_4$OH-4, C$_6$H$_4$OMe-4, C$_6$H$_4$Me-4, Ph, C$_6$H$_4$F-4, C$_6$H$_4$Cl-4, ^{i}Pr, ^{t}Bu, Me or CH$_2$C$_6$H$_4$Cl-4]. These complexes, denoted as *cis*$^+$ and *trans*$^+$, undergo, as observed for the above chloro-mononitrile complex, two successive single-electron oxidations to form the 17-electron (*cis*$^{2+}$ or *trans*$^{2+}$) and 16-electron (*cis*$^{3+}$ or *trans*$^{3+}$) derivatives, (Scheme 5 and Fig. 6 for R = C$_6$H$_4$NEt$_2$-4) at oxidation potentials that are higher for the *cis* isomers, $E°(cis^{+/2+}) = 0.29–0.55$ V and $E°(cis^{2+/3+}) = 1.09–1.52$ V vs. SCE, than for the corresponding *trans* ones, $E°(trans^{+/2+}) = 0.11–0.46$ V and $E°(trans^{2+/3+}) = 0.99–1.47$ V vs. SCE [48]. The *cis*$^{3+}$ complexes isomerize to the *trans*$^{3+}$ homologues which undergo a slower decomposition reaction, and the rate constants (k_3 and k_{dec} for the isomerization and decomposition, respectively) were determined by kinetic analysis (digital simulation) of the cyclic voltammetric behavior, and are shown to respond to electronic and steric effects.



Scheme 5. Double square scheme for redox induced *cis*/*trans* isomerization for $[Re(NCR)_2(dppe)_2]^+$ [48].

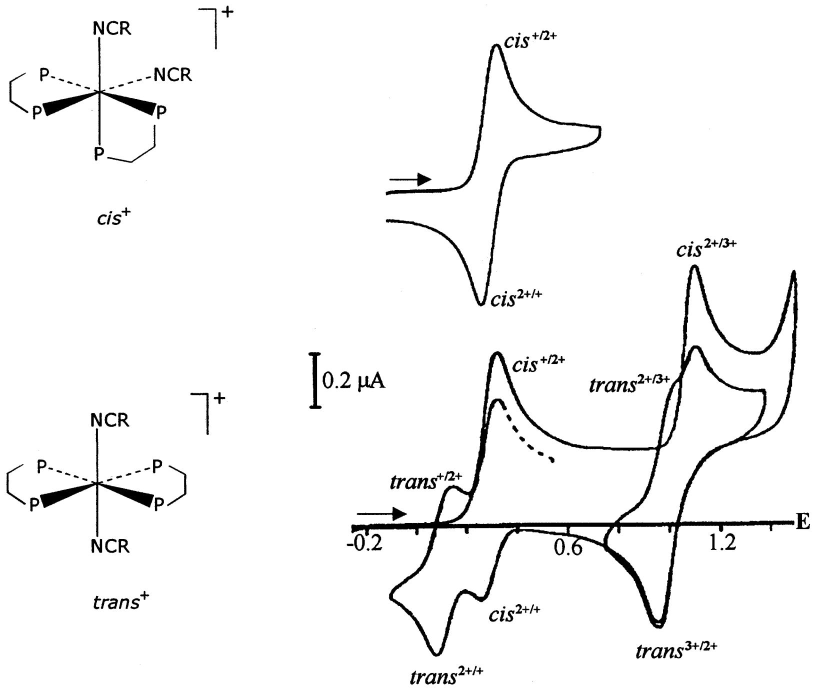


Fig. 6. Cyclic voltammogram for *cis*-$[Re(NCC_6H_4NEt_2\text{-}4)_2(dppe)_2[BF_4]$ (1.1 mM) in CH_2Cl_2 with 0.2 with $[NBu_4][BF_4]$, at 25°C and at a Pt disc electrode (0.5 mm diameter) at a scan rate of 0.20 V s^{-1}. In the upper voltammogram the scan was reversed after the first oxidation wave. Potential in volts vs. SCE [48].

For the *aromatic* nitrile complexes both rate constants ($k_3 = 0.4 \times 10^2$–25×10^2 s^{-1}, $k_{dec} = 0.25$–1.8 s^{-1}) increase with the electron-withdrawing ability of R as measured by the Hammett's σ_p constant [48]. The promotion of the rate of the $cis^{3+} \rightarrow trans^{3+}$ isomerization by a decrease of the electron-release from the nitrile ligand to the metal center corresponds to a weakening of the metal–phosphine and metal–nitrile bonds, thus favoring an intramolecular twist mechanism for the isomerization. Such a rationalization is also in agreement with the much higher propensity for the ET-induced isomerization of the carbonyl compound *cis*-$[ReCl(CO)(dppe)_2]$ (see below), in comparison with the nitrile complexes *cis*-[Re-

Cl(NCR)(dppe)$_2$] and *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$; in the CO compound, the 17-electron level (single oxidation) is sufficient for the isomerization [rate constant ($cis^+ \rightarrow trans^+$) = 80 s^{-1} at 0°C] [49], whereas for the nitrile complexes the isomerization still does not occur (e.g. rate constant $< 10^{-4}$ s^{-1} at 25°C for the dinitrile complexes) [48] and requires further oxidation to the 16-electron level.

The enhancement of the rate of decomposition of $trans^{3+}$ (dinitrile complexes) upon increasing the electron-withdrawing ability of the R group suggests that the decomposition process involves a nucleophilic addition to the metal or to the ligated nitriles.

However, the *alkyl* nitrile complexes isomerize at rates ($k_3 = 10 \times 10^2 - 13 \times 10^2$ s^{-1}) that are not slower than those of the aromatic ones due to steric effects which display a dominant role in the former, favoring the *trans* geometry mainly at the higher metal oxidation state, Re(III), when π-electronic effects are hampered, providing a further driving force for the *cis*-to-*trans* isomerization [48].

In contrast with the above chloro-mononitrile compound [ReCl(NCR)(dppe)$_2$] [36] and with the Group 6 dicarbonyl complexes [M(CO)$_2$(LL)$_2$] (M = Cr, Mo, W; LL = diphosphine) [25,29,30,32], the *trans* isomers of [Re(NCR)$_2$(dppe)$_2$]$^{n+}$ (n = 1–3) are thermodynamically more stable than the homologous *cis* ones, not only in the oxidized forms but also at the low redox level in the 18-electron configuration [$K_1(cis^+ \rightleftarrows trans^+) > 10$] [48]. However, kinetic constraints impose that the *cis*-to-*trans* isomerization only occurs effectively, under the experimental conditions used, at the dioxidized level (kinetic gain upon oxidation). The high thermodynamic gain towards the *trans* isomeric forms resulting from a single-electron oxidation ($K_2/K_1 = 33 - 1.1 \times 10^3$ for the aromatic dinitrile complexes) was not sufficient to induce the isomerization. A lower thermodynamic gain occurs upon the second oxidation (K_3/K_2 = 1.5–49) [48].

The ratios of the isomeric equilibrium constants at the various redox states and the redox potentials, within the arylnitrile complexes, were shown to follow the electronic properties of the R group of the ligated nitriles as indicated by the recognized linear relationships [48] of ln(K_2/K_1), ln(K_3/K_2) or ln(K_3/K_1) vs. Hammett's σ_p constant (for the substituent of the phenyl ring) and of $E°$ (for each redox couple along the isomeric series, i.e. $trans^{+/2+}$, $trans^{2+/3+}$, $cis^{+/2+}$ or $cis^{2+/3+}$) vs. the same Hammett's constant. The results are indicative of a stronger π-electron acceptance of the *trans* nitriles with a greater participation in delocalized π-electronic systems than the *cis* nitriles, and of a greater sensitivity of the *trans* isomers, in comparison with the *cis* ones, to an electronic change of the nitrile [48].

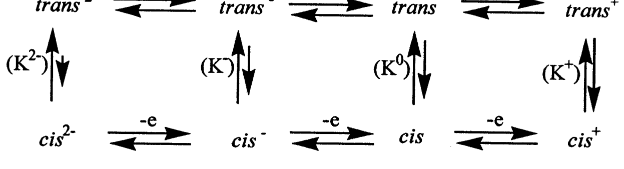
The above systems comprise anodically induced *cis*-to-*trans* isomerizations, but in isomeric redox couples with reversed relative isomeric stabilities the opposite can occur, i.e. an anodically promoted *trans*-to-*cis* isomerization. An example involving an extended (ladder-type) square scheme (whose kinetics however were not investigated) is provided by the redox series [Os(N$_2$O$_2$)L$_2$]^n [N$_2$O$_2$ = basic form (tetraanionic) of 1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene; L = *p*-substituted pyridine; n = 2− to 1+], in which the polyanionic *N*-amido species (N$_2$O$_2$) acts as a tetrahapto strong electron-donor ligand, chelating the metal via the two amido- and the two oxy-atoms [50]. The complexes present the *trans* and/or the *cis*-α stereochemistries, the former containing planar *N*-amido ligands (in the N_2O_2 chelating ligand), whereas a non-planar structure for these ligands occurs in the latter isomer (onwards simply denoted by *cis*, in which the two O atoms are *trans* to each other).

The *trans* isomers are oxidized at higher potentials than the *cis* ones, and thus (see Eq. (1)) oxidation favors the *cis* relative to the *trans* forms as indicated by the estimated values of the isomeric equilibrium constants. The starting member of the redox series (see the extended square scheme (Scheme 6)) is the neutral 16-electron *trans* Os(IV) complex, and the equilibrium constant (K^+ ca. 1) for the $cis^+ \rightleftarrows trans^+$ process, involving the electrogenerated cationic 15-electron Os(V) complexes (derived from the corresponding *trans* compounds), has been measured by normal pulse voltammetry and used with the oxidation potentials for the three successive reductions of cis^+ and $trans^+$ to estimate the isomeric equilibrium constants at the Os(IV), Os(III) and Os(II) oxidation levels, i.e. $K^0 = [trans]/[cis] \cong 10^3$, $K^- = [trans^-]/[cis^-] \cong 10^{11}$ and $K^{2-} = [trans^{2-}]/[cis^{2-}] \cong 10^{15}$, respectively [50].

Hence, the *trans* form is progressively less favored upon stepwise oxidation until at the cationic 15-electron level the *cis* isomer has a comparable stability and a *trans*-to-*cis* isomerization occurs.

Such a thermodynamic behavior has been interpreted [50] by considering that the *trans*-to-*cis* conversion involves a planar-to-non-planar isomerization of the *N*-amido ligands whose non-planar form behaves as an even stronger electron donor than the planar one (which is the one present in the *trans* isomers); this also accounts for the lower oxidation potentials of the *cis* relative to the *trans* isomers in these systems.

The $K°(cis \rightleftarrows trans)$ equilibrium constant was shown to correlate with the σ_p-substituted constant (for the pyridine substituent in the ancillary L ligand) and with the Fischer $\bar{\sigma}$ substituent constant for pyridinium ion dissociations: $\log K^0$ decreases in a grossly linear way with the increase of these constants, i.e. when L becomes less electron donating the equilibrium favors the stronger electron releasing *cis* arrangement (see above), compensating in this way the metal for the decrease of the electron release from L [50]. Hence, the K^0 equilibrium responds to electronic effects of the ligands. Consistent with this behavior is the observed isomeric shift towards the *cis* isomer on replacement of the pyridine ligand by a π-electron acceptor such as an isocyanide (L = CN^{t}Bu) when such an isomeric form becomes the thermodynamically stable one at the neutral Os(IV) stage [50].

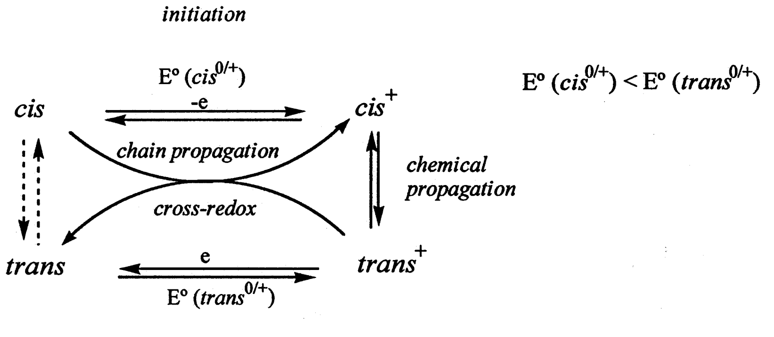


Scheme 6. Triple square scheme for the redox series *trans*/*cis*-$[Os(N_2O_2)L_2]^n$ ($n = 2-$ to $1+$) [50].

2.3. ETC-catalyzed isomerization

In the situations of anodically induced A-to-B isomerization (A is the starting form) described above, the ET-generated isomer (B^+ derived from isomerization of A^+) belongs to a redox couple (B/B^+) with a lower redox potential than that of A/A^+, i.e. $E°(B/B^+) < E°(A/A^+)$. In particular, for the anodically promoted *cis*-to-*trans* isomerization, the *trans* isomer is oxidized at a lower potential than the *cis*, $E°(trans^{0/+}) < E°(cis^{0/+})$ (Scheme 1). However, if the opposite situation holds, i.e. $E°(trans^{0/+}) > E°(cis^{0/+})$, the *trans*$^+$ product should be reduced by the electrode at the potential, $E°(cis^{0/+})$, it is generated to give the reduced *trans* form. The overall process, although triggered by the anodic ET, results in the formation of the reduced form of the *trans* isomer without an overall redox change (Scheme 7). It is catalyzed by the electron and corresponds to an ETC catalyzed process that can be denoted by $\vec{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ ($\vec{\mathrm{E}}$ is the initiation step by ET; C is the chemical propagation step and $\overleftarrow{\mathrm{E}}$ is the "back ET", the second propagation step which can occur at the electrode or in solution). Although this process can be analyzed by a square scheme of the general type of those presented above, its peculiar features justify a separate discussion.

This is illustrated by the chloro-carbonyl *cis*-/*trans*-[ReCl(CO)(dppe)$_2$] couple which has been studied electrochemically in great detail [49]. The *cis* isomer is oxidized at a lower potential than the *trans* one, in contrast with the above-mentioned dicarbonyls [M(CO)$_2$(LL)$_2$] (M = Cr, Mo, W; LL = diphosphine), and the π-electron donor Cl ligand in the former plays a relevant role in the reverse of the HOMO energies of the two isomers by destabilizing the metal d_{xy} orbital only in the *cis* isomer, as accounted for by the qualitative d_π orbital-level splitting shown in Fig. 7 for complexes of the general type [MXYL$_4$] (X = strong π-electron donor, Y = strong π-electron acceptor, L = 2e-donor ligand that is neither a π-electron donor nor a strong π-electron acceptor, i.e. in the present case M = Re, X = Cl, Y = CO, L = $\frac{1}{2}$dppe) [49]. The stabilizing effect on the metal d_π orbitals resulting from the strong π-electron acceptor (Y = CO, π* orbitals) is opposed by the destabilizing interaction with the π-electron donor (X = Cl, p orbitals) and the difference between the number of destabilizing interactions and the number of stabilizing ones is denoted by x.



Scheme 7. ETC-catalyzed *cis*/*trans* isomerization process ($\vec{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$).

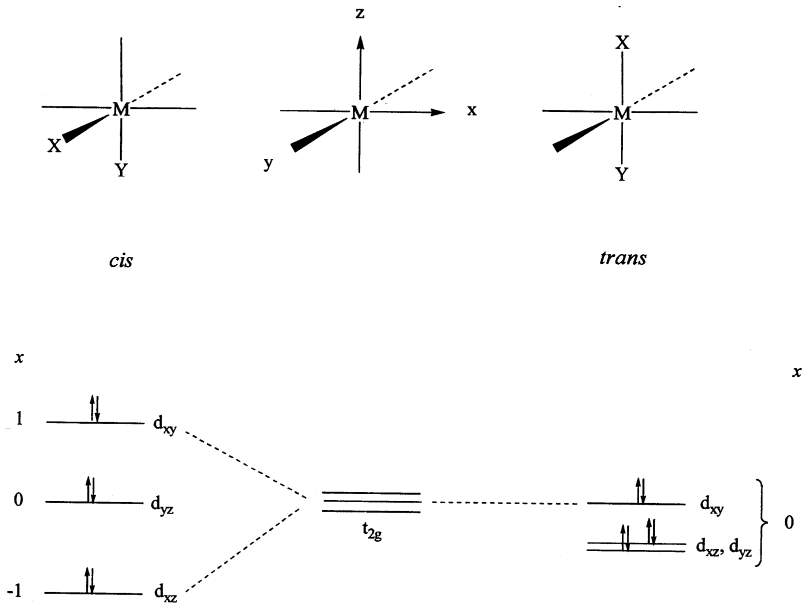
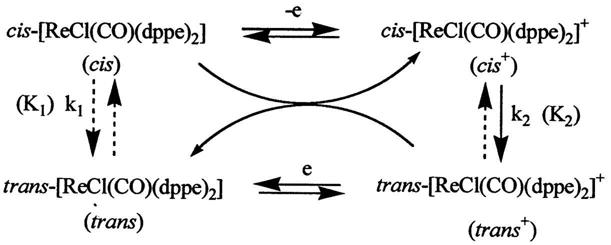
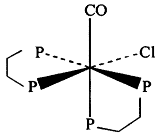


Fig. 7. d_π oribtal level splitting for isomers of [$MXYL_4$] where X = strong π-electron donor, Y = strong π-electron acceptor, L = 2e-donor ligand that is neither a π-electron donor nor a strong π-electron acceptor (x is the difference between the number of destabilizing interactions with filled X orbitals and the number of stabilizing interactions with empty Y orbitals (in the *trans* isomer, the relative positions of the d_{xz}, d_{yz} and d_{xy} orbitals are shown arbitrarily). The indicated filling of orbitals corresponds to a d^6 metal complex. [49].

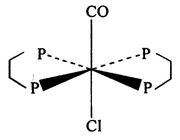


Scheme 8. ETC-catalyzed *cis*/*trans* isomerization of *cis*-[ReCl(CO)(dppe)$_2$ [49].

The anodic ETC-catalytic isomerization undergone by *cis*-[ReCl(CO)(dppe)$_2$] (denoted by *cis*) is depicted in Scheme 8 and examples of cyclic voltammograms (experimental and simulated ones) are given in Fig. 8 [49]. Oxidation to *cis*$^+$ is followed by isomerization to *trans*$^+$ which is either reduced by the electrode (at the potential it is generated) to give *trans* or oxidizes, in an homogeneous way (redox cross reaction), the *cis* isomer to form *cis*$^+$ and *trans* [Eq. (5), the reverse of Eq. (3)]. Therefore, the non-oxidized *trans* isomer, *trans*-[ReCl(CO)(dppe)$_2$], is formed in both heterogeneous and homogeneous ways and the overall isomerization is catalytic in electrons [49].



cis



trans

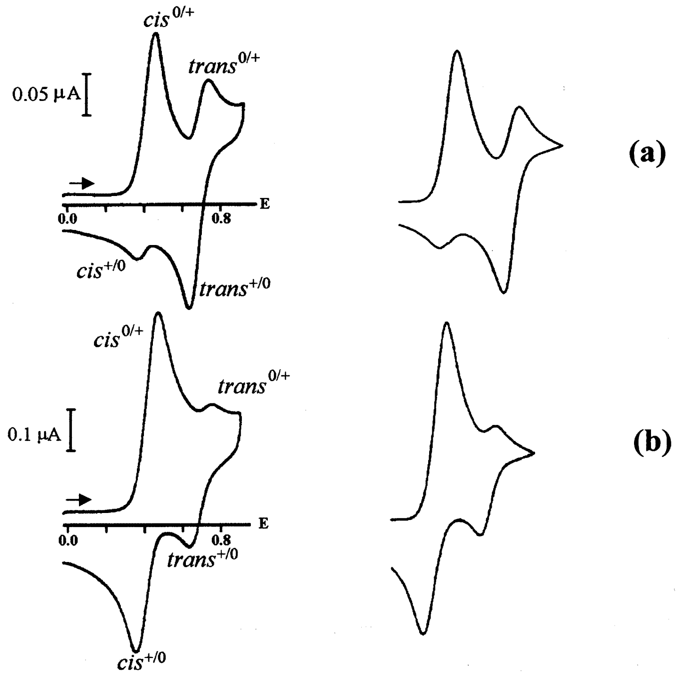


Fig. 8. Experimental (left) and simulated (right) cyclic voltammograms for *cis*-[ReCl(CO)(dppe)$_2$] (0.6 mM) in CH_2Cl_2 with 0.2 M [NBu_4][BF_4], at −40°C and at a Pt disc electrode (0.5 mm diameter). Scan rate of: (a) 0.2 and (b) 0.8 V s^{-1}. Potential in volts vs. SCE [49].

$$trans^{+} + cis \rightleftarrows trans + cis^{+} \tag{5}$$

The rate of $cis^{+} \rightarrow trans^{+}$ isomerization was estimated for various temperatures (e.g. $k_2 = 0.85$ or 80 s^{-1} at −40 or 0°C, respectively) [49] and is shown to be much higher than that (well below 10^{-4} s^{-1} at 0°C) [47] for the isomerization of the related nitrile complex *cis*-[ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$]$^{+}$, indicating a much higher propensity of the carbonyl complex for isomerization in accord with the strong π-electron-withdrawing ability of CO with a resulting labilization of the metal–phosphine bonds, favorable to the geometrical rearrangement.

The reverse in the order of the redox potential of the isomers, as discussed above, $E°(cis^{0/+}) < E°(trans^{0/+})$, results (Eq. (1)) in a very low ratio of the isomeric equilibrium constants for the oxidized and neutral species, $K_2([trans^{+}]/[cis^{+}])/K_1([trans]/[cis]) = (1.5 \pm 0.7) \times 10^{-6}$ at −40°C that is the inverse of the equilibrium constant of the cross redox reaction (5) [49]. Hence, oxidation does *not* lead to a shift of the isomerization equilibrium towards the *trans* geometry, i.e. the cross redox equilibrium (5) lies towards the *trans* and *cis*$^+$ species (the estimated forward and backward rate constants are $k = (9 \pm 2) \times 10^3$ M^{-1} s^{-1} and $k_- = (1.3 \pm 0.9) \times 10^{-2}$ M^{-1} s^{-1}, at -40°C] [49], in contrast with the case of the abovementioned dicarbonyl or nitrile complexes. Nevertheless, the *cis*$^+ \rightarrow$ *trans*$^+$ isomerization occurs on account of the effects of the other reactions (e.g. consumption of the generated *trans*$^+$ by electrode reduction and by *cis*) and of kinetic promotion on oxidation [49]. The isomeric conversion of *cis* into *trans*, by controlled potential electrolysis at the anodic wave of *cis*, was fast and involved a very small current and charge, being completed after the consumption of less than 0.018 F mol^{-1} (coulombic efficiency greater than 56) [49].

Following the pioneering work of various groups [51–54], ETC catalysis is gaining an increasing interest in both coordination chemistry and electrochemistry (the field has been reviewed [1,28b,55]) and a variety of reaction types has already been electrocatalyzed, mainly comprising ligand exchange [56] and, less commonly, ligand insertion [57] or extrusion [58]. However, examples of electrocatalyzed isomerizations or other structural rearrangements are less known and they involve, besides the one discussed above, namely di- or poly-carbonyl complexes, e.g. of molybdenum or tungsten [59], manganese [60], cobalt [61] and rhodium [62], and a cobalt/iridium carbonyl cluster [11a].

3. *Fac/mer* isomerization

Various *fac/mer* couples of tricarbonyl complexes of Group 6 transition metals, $[M(CO)_3L_3]^{0/+}$ (M = Cr, Mo or W; L = phosphine, phosphite, isocyanide, etc.) have been investigated electrochemically and behave similarly to what was observed (see above) for the *cis/trans* couple of related dicarbonyl complexes $[M(CO)_2L_4]^{0/+}$. Hence, the neutral 18-electron *fac* isomer is oxidized at a higher potential than the *mer* one, in agreement with some semiempirical predictions [17] (Fig. 9) and oxidation of the former can induce geometrical isomerization to give *mer*$^+$, according to the square scheme (Scheme 9) (for the charge $z = 0$) which is analogous to that (Scheme 1) discussed above for the *cis/trans* couple. Let us consider examples of this behavior as well as some cases in which deviations are observed namely due to stereochemical factors.

Variable temperature voltammetric studies and controlled-potential electrolysis for the *fac/mer*-$[Cr(CO)_3L_3]^{0/+}$ [L = P(OMe)$_3$] system allowed one to estimate [36] the thermodynamic and kinetic constants: $K_1 = k_1/k_{-1} = 1.8 \times 10^{-4}$ s^{-1}/4.5×10^{-5} s$^{-1} \cong 4$ and $K_2 = k_2/k_{-2} = 0.11$ s^{-1}/1.7×10^{-4} s$^{-1} \cong 6 \times 10^2$. Hence, the 17-electron *mer*$^+$ isomer is much more favored with respect to *fac*$^+$ than the 18-electron *mer* over the *fac* one ($K_2/K_1 \cong 1.5 \times 10^2$). Moreover, the isomerization rate in either direction is enhanced for the 17-electron configuration relatively to the corresponding one for the 18-electron species ($k_2 \gg k_1$, $k_{-2} > k_{-1}$).

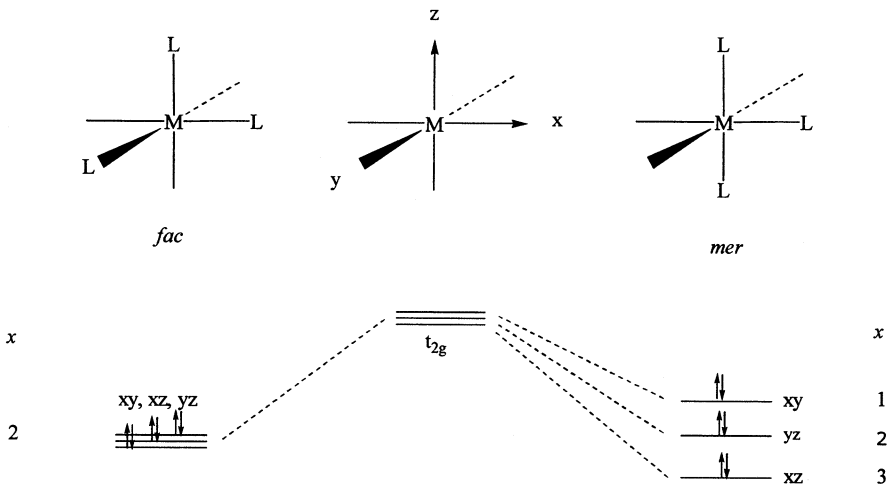
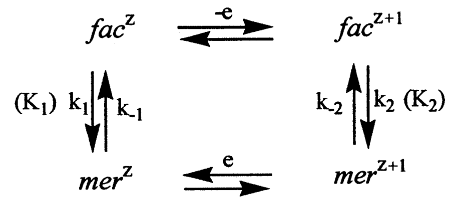


Fig. 9. d_π orbital level splitting for the *fac* and *mer* isomers of $[ML_3L'_3]$ where L is a better π-acceptor than L′ (*x* is the number of L ligands that can interact with a given metal d_π orbital) (adapted from Ref. [17]). The filling of orbitals corresponds to the d^6 metal complexes.



Scheme 9. Square scheme for redox induced *fac*/*mer* isomerizations.

The activation parameters for the $fac^+ \rightleftarrows mer^+$ isomerization are consistent with an intramolecular twist mechanism. Besides the slow $fac \rightarrow mer$ isomerization by such a type of mechanism, an alternative and fast redox-catalyzed pathway has also been detected [36] at an early stage of the oxidative electrolysis of *fac*, which has been explained in terms of the redox cross-reaction between the electrogenerated mer^+ and the starting *fac* complex, i.e. $fac + mer^+ \rightleftarrows fac^+ + mer$, in spite of this reaction being thermodynamically unfavorable.

The model complexes *fac*- and *mer*-$[Cr(CO)_3L_3]$ [L = PH_3 or $P(OH)_3$], as well as the related *cis* and *trans* isomers of $[Cr(CO)_2L_4]$ and $[Cr(CO)_4L_2]$ (see Section 2.1), were the object of an extended Hückel study which, although consistent with the relative values of the oxidation potential, could not be applied with confidence to the prediction of the relative stability of the isomers as a result of the strong dependence on the bond lengths used for the calculations [31].

Another system that follows the above square scheme (Scheme 9) (for $z = 0$) comprises the mixed carbonyl–isocyanide *fac*/*mer*-$[Mo(CO)_3(CNR)_3]$ (R = $C_6H_3Me_2$-2,6) complexes [63]. The *fac* isomer oxidizes at a higher potential than the *mer* one, in agreement with some predictions (Fig. 9) and then undergoes isomerization to the latter isomer, i.e. $fac^+ \rightarrow mer^+$. Digital simulation of the cyclic voltammogram and IR spectroscopic measurements confirmed the isomerization, and the rate constants for the conversions, $fac^+ \rightarrow mer^+$ ($k_2 = 7$ s^{-1}) and $mer \rightarrow fac$ ($k_{-1} =$ 0.8 s^{-1}), have been estimated [63]. The related *cis*/*trans*-[Mo(CO)$_2$(CNR)$_4$] couple behaves electrochemically in a similar way, although presenting slower kinetics: k_2 ($cis^+ \rightarrow trans^+$) = 0.09 s^{-1} and k_{-1} ($trans \rightarrow cis$) = 0.14 s^{-1} [63].

A systematic study on the influence of chelating phosphine [38,64–66] or arsine [64] ligands on the electrochemical behavior of tricarbonyl Cr, Mo or W complexes has appeared.

In the case of complexes containing a pendant diphosphine (diarsine or mixed phosphine–arsine), upon electrochemical oxidation the pendant P (or As) atom can act as an "internal" nucleophile towards the metal. Hence, e.g. oxidation of *fac*- or *mer*-[M(CO)$_3$(η^1-LL)(η^2-LL)] (M = Mo or W, LL = dppe or dppm) upon an overall two-electron process produces the seven coordinate 18-electron M(II) complexes [M(CO)$_3$(η^2-LL)$_2$]$^{2+}$ which are formed via the M(I) intermediate mer^+ complex (derived either from oxidation of *mer* or from oxidation of *fac* followed by the expected $fac^+ \rightarrow mer^+$ isomerization) [65,67]; the coordination of the pendant phosphorus atom, induced by oxidation, allows the re-establishment of the 18-electron configuration to the complex. The mer^+ intermediates with dppe ligands are relatively stable, but those with dppm rapidly disproportionate to the corresponding M(0) and M(II) complexes, thus showing the significance of the chelate ring size [65].

Moreover, the Cr(I) complexes *mer*-[Cr(CO)$_3$(η^1-LL)(η^2-LL)]$^+$ (LL = dppm [66], Ph$_2$PNHPPh$_2$ (dppa) [66], Ph$_2$PN(Me)PPh$_2$ (dppma) [66], Ph$_2$PCH$_2$CH$_2$AsPh$_2$ (ape) [64] or Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ (dae) [64]) denoted by mer^+, electrochemically generated by single-electron oxidation of the corresponding *mer* or *fac* complexes (in the latter case via the anodically induced $fac^+ \rightarrow mer^+$ isomerization), convert into *trans*-[Cr(CO)$_2$(η^2-LL)$_2$]$^+$, as shown by EPR spectroscopy [64]. The replacement of a carbonyl ligand by the pendant P (or As) group, a better net electron-donor than CO, partially compensates for the loss of electron density at the metal upon oxidation, although with retention of the 17-electron configuration. This behavior is consistent with the known usually faster CO substitution reactions for 17-electron complexes in comparison with the corresponding 18-electron species [38].

An unusual isomeric *fac*/*mer* lability has been reported for the sterically constrained systems [M(CO)$_3$(η^3-triphos)]$^{0/+}$ (M = Cr, Mo or W), in which the 17-electron fac^+ and mer^+ isomers are of comparable stability [38].

The systems were studied by both conventional and fast (using microelectrodes) cyclic voltammetry, at variable temperature, and their behavior was accounted for by the square reaction scheme (Scheme 9) (for the charge $z = 0$). Digital simulation has allowed one to estimate the equilibrium and rate constants. Interestingly, in these systems the fac^+ isomer for W is the thermodynamically preferred one relatively to mer^+ ($K_2 = [mer^+]/[fac^+] < 1$), no isomeric preference is observed for Mo ($K_2 \cong 1$), or the mer^+ isomer is only weakly favored for Cr ($K_2 \cong 3.2$) [38]. This contrasts with the normal situation in which the mer^+ isomer is strongly favored relative to *fac*$^+$ (see above), as observed, e.g. for $[Cr(CO)_3\{P(OMe)_3\}_3]$ ($K_2 = 6.3 \times 10^2$) [36].

Moreover, the kinetics of all the isomerization steps are exceptionally fast, and the corresponding rate constants are several orders of magnitude higher than those, inter alia, for that phosphite chromium complex, e.g.: $k_2(fac^+ \rightarrow mer^+) = 5.0 \times 10^2$ (M = Cr) or 1.2×10^3 (M = Mo) s^{-1} for the η^3-triphos complexes, and 1.1×10^{-1} s^{-1} for the phosphite compound; k_{-1} ($mer \rightarrow fac$) = 77 (M = Cr) or 1.0×10^3 (M = Mo) s^{-1} for the η^3-triphos complexes and 4.5×10^{-5} s^{-1} for the phosphite compound [38]. This rapid isomeric conversion is tentatively explained [38] by considering that both isomeric forms are highly strained structures within the tridentate triphos ligand (as a result of either interactions of some of the phenyl groups or strains in five-membered chelate rings). The ligand effect on those thermodynamic or kinetic variations largely overcomes that of the metal (only relatively small changes result upon changing the metal in the triphos system).

The related Mn complexes *cis,mer*-$[MnX(CO)_2(\eta^3\text{-triphos})]$ (X = Cl or Br) undergo an anodically induced *cis*-to-*trans* isomerization ($cis^+ \rightarrow trans^+$) but, since it is slow, it allows the observation, at low temperature, of the *mer*-to-*fac* isomerization, i.e. $cis,mer^+ \rightarrow cis,fac^+$ [34]. This mer^+/fac^+ isomerization is fast in both directions [34] as observed (see above) for the $[M(CO)_3(\eta^3\text{-triphos})]^+$ (M = Cr, Mo or W) systems, but no kinetic studies were reported. Single electron oxidation of the Mn(I) complexes *fac*-$[Mn(phen)(CO)_3L]^+$ (phen = phenanthroline, L = imidazole or derivative) also induces the formation of the corresponding *mer* isomers, but no kinetic investigation is provided [68].

Redox-induced *fac*/*mer* isomerization is also known for systems without π-electron acceptor ligands, such as the trischelates $[M(\overset{\frown}{N\,O})_3]^{0/-}$ (M = Mn [69], Fe [70] (the anionic forms being analogues of ferroverdin, a green biological pigment) or Ni [71]; $\overset{\frown}{N\,O}$ = = substituted quinone-2-oximate) with trivalent/divalent metal, respectively.

The electrochemical behavior has been investigated by variable temperature differential pulse voltammetry and cyclic voltammetry, and described by Scheme 9 (for the charge $z = -1$).

The fac^- isomers are oxidized at higher potentials than the corresponding mer^- complexes, and the isomerization equilibrium constants have been estimated from the electrochemical measurements, whereas the rates of isomerizations could be obtained spectrophotometrically.

Since the divalent fac^- isomers are oxidized at higher potentials than the corresponding mer^- complexes, the isomerization equilibrium constant for the trivalent neutral complexes (K_2) should be greater (see Eq. (1) adapted to the present case) than that for the divalent species (K_1). In fact, K_2/K_1 ca. 4×10^3 (M = Mn), ca. 2×10^3 (M = Fe) or ca. 6×10 (M = Ni); moreover, K_1 is much lower (by ca. three orders of magnitude) for the iron system (K_1 ca. 5×10^{-3}) than for the other metals. These trends have been accounted for tentatively [69] by steric, electrostatic or electronic factors, with a dominant stabilizing effect on the trivalent *mer*, the divalent fac^- or the divalent d^6 fac^- [i.e. Fe(II)] isomers, respectively. The rate constants (k_2) for the $fac \rightarrow mer$ isomerization have also been estimated as ca. 0.03 s^{-1} (M = Mn at 260 K) [69], 0.02 s^{-1} (M = Ni, at 258 K) [71] or ca. 5×10^{-4} s^{-1}

(M = Fe, at 292 K) [70], thus the iron complex undergoing the slower isomerization. This is suggested [69] to involve an intramolecular twist pathway.

4. Prospects and outlook

The behavior of coordination compounds that can exist in two geometrical forms, typically *cis* and *trans* or *fac* and *mer* isomers, whose relative stability is dependent on the metal oxidation state (electronic count), can be investigated adequately by electrochemical methods if the redox processes involved for both forms occur at distinct potentials. The difference in the redox potentials of the two isomeric redox couples is a determinant factor of the relative isomeric stability, which thus depends on all the factors that influence the redox potential, namely the structure and composition of the complexes, in particular the electronic configuration, the metal oxidation state, the electron donor/acceptor character of the ligands and steric factors. Rationalizations of the differences of the redox potentials for isomeric redox pairs have been proposed for some types of complexes on the basis of simplified orbital level splittings, but their application has not yet been extended to all the possible situations, in particular with strong π-electron donor ligands, and systematic theoretical quantum chemical calculations are still lacking.

ET can induce the isomerization reaction by promoting the conversion of an isomer into the other provided the relative stability of the latter is favored on oxidation or reduction of the former. Moreover, the kinetics can also be dramatically sped up. However, in some systems a single-ET is not sufficient for the occurrence of the isomerization and a further ET is required.

The study of the mechanism of the isomerization step itself has been addressed only rarely and points towards an intramolecular twist process rather than a dissociation (metal–ligand cleavage) one, but the limited number of cases investigated do not allow generalizations.

The overall redox processes can be analyzed in terms of square ECEC mechanisms whose thermodynamics and kinetics have been investigated in detail in a few cases and eventually shown to respond to both electronic and steric effects, being determined by a delicate balance between them, which has not yet been fully understood. Nevertheless, in a set of closely related complexes, the lability towards isomerization appears to follow the increase of the net electron acceptor character of the ligands, and complexes with the strong π-electron acceptor carbonyl ligands have been the most studied. However, the use as ligands of weaker π-acids (e.g. organonitriles) or even π-electron donors (e.g. chloride) results in a different behavior, namely requiring two ETs in double-square schemes, and the subsequent extension to multi-ET systems following extended square-type processes is expected to be achieved. Of particular significance would be the development of systems with molecular hysteresis behavior in which the stable states would be represented by the more stable isomeric forms at different redox levels.

Further exploration of ETC catalytic isomerization processes is required (only a very limited number of examples is known), in view of their significance in terms of accomplishing an isomerization reaction without an overall redox change (the new isomer lies at the same redox level as the parent one) and with a minimum energy requirement.

Acknowledgements

This work has been partially supported by the National Board for Scientific and Technological Research (JNICT), the Foundation for Science and Technology (FCT) and the PRAXIS XXI Programme. The authors also gratefully acknowledge Dr. C. Amatore (École Normale Supérieure, Paris) for stimulating discussions, cooperation and training on digital simulation methods, and Prof. J.J.R. Fraústo da Silva (Centro de Química Estrutural, Instituto Superior Técnico, Lisboa) for general support.

References

[1] D. Astruc, Electron Transfer and Radical Processes in Transition-Metal Chemistry, VCH Publishers, New York, 1995.

[2] A.J.L. Pombeiro, J. McCleverty (Eds.), Molecular Electrochemistry in Inorganic, Bioinorganic and Organometallic Compounds, NATO ASI Series, Kluwer Academic, Dordrecht, 1993.

[3] W.E. Geiger, Prog. Inorg. Chem. 33 (1985) 273.

[4] W.C. Trogler (Ed.), Organometallic Radical Processes, J. Organomet. Chem. Lib. 22 (1990).

[5] (a) N.G. Connelly, Chem. Soc. Rev. 18 (1989) 153. (b) N.G. Connelly, W.E. Geiger, Adv. Organomet. Chem. 23 (1984) 1.

[6] A.M. Bond, R. Colton, Coord. Chem. Rev. 166 (1997) 161.

[7] W.E. Geiger, Acc. Chem. Res. 28 (1995) 351.

[8] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.

[9] A.J.L. Pombeiro, Portug. Electrochim. Acta 1 (1983) 19.

[10] (a) J. Ruiz, F. Ogliaro, J.-Y. Saillard, J.-F. Halet, F. Varret, D. Astruc, J. Am. Chem. Soc. 120 (1998) 11693. (b) M. Lacoste, F. Varret, L. Toupet, D. Astruc, J. Am. Chem. Soc. 109 (1987) 6504. (c) R.M. Nielson, M.J. Weaver, Organometallics 8 (1989) 1636. (d) T. Roth, W. Kaim, Inorg. Chem. 31 (1992) 1930.

[11] (a) W.E. Geiger, M.J. Shaw, M. Wünsch, C.E. Barnes, F.H. Foersterling, J. Am. Chem. Soc. 119 (1997) 2804. (b) M.-H. Delville-Desbois, S. Mross, D. Astruc, J. Linares, F. Varret, H. Rabaâ, A. Le Beuze, J.-Y. Saillard, R.D. Culp, D.A. Atwood, A.H. Cowley, J. Am. Chem. Soc. 118 (1996) 4133. (c) M.-H. Delville-Desbois, S. Mross, D. Astruc, Organometallics 15 (1996) 5598. (d) D.W. Powell, P.A. Lay, Inorg. Chem. 31 (1992) 3542. (e) W.D. Harman, M. Sekine, H. Taube, J. Am. Chem. Soc. 110 (1988) 2439. (f) W.D. Harman, H. Taube, J. Am. Chem. Soc. 110 (1988) 5403. (g) W.D. Harman, J.F. Wishart, H. Taube, Inorg. Chem. 28 (1989) 2411.

[12] (a) D.T. Pierce, T.L. Hatfield, E.J. Billo, Y. Ping, Inorg. Chem. 36 (1997) 2950. (b) N.M. Villeneuve, R.R. Schroeder, L.A. Ochrymowycz, D.B. Rorabacher, Inorg. Chem. 36 (1997) 4475. (c) P.V. Robandt, R.R. Schroeder, D.B. Rorabacher, Inorg. Chem. 32 (1993) 3957. (d) D.J. Cárdenas, A. Livoreil, J.-P. Sauvage, J. Am. Chem. Soc. 118 (1996) 11980. (e) A. Livoreil, C.O. Dietrich-Buchecker, J.-P. Sauvage, J. Am. Chem. Soc. 116 (1994) 9393.

[13] J.A. Wytko, C. Boudon, J. Weiss, M. Gross, Inorg. Chem. 35 (1996) 4469.

[14] (a) L.F. Szczepura, S.A. Kubow, R.A. Leising, W.J. Perez, M.H.V. Huynh, C.H. Lake, D.G. Churchill, M.R. Churchill, K.J. Takunchi, J. Chem. Soc. Dalton Trans. (1996) 1463. (b) A. Tomita, M. Sano, Inorg. Chem. 33 (1994) 5825. (c) M. Sano, H. Taube, Inorg. Chem. 33 (1994) 705. (d) M.

Sano, H. Taube, J. Am. Chem. Soc. 113 (1991) 2327. (e) T. Roth, W. Kaim, Inorg. Chem. 31 (1992) 1930.
[15] N.G. Connelly, W.E. Geiger, M.C. Lagunas, B. Metz, A.L. Rieger, P.H. Rieger, M.J. Shaw, J. Am. Chem. Soc. 117 (1995) 12202.
[16] (a) R.D. Moulton, D.J. Chandler, A.M. Arif, R.A. Jones, A.J. Bard, J. Am. Chem. Soc. 110 (1988) 5714. (b) J.G. Gaudiello, T.C. Wright, R.A. Jones, A.J. Bard, J. Am. Chem. Soc. 107 (1985) 888.
[17] B.E. Bursten, J. Am. Chem. Soc. 104 (1982) 1299.
[18] D.L. Dubois, R. Hoffmann, Nouv. J. Chim. 1 (1977) 479.
[19] J.N. Murrell, A. Al-Derzi, G.J. Leigh, M.F. Guest, J. Chem. Soc. Dalton Trans. (1980) 1425.
[20] D.M.P. Mingos, J. Organomet. Chem. 179 (1979) C29.
[21] M.F.C. Guedes da Silva, M.T. Duarte, A.M. Galvão, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Organomet. Chem. 433 (1992) C14, and references therein.
[22] T.A. George, R.K. Hayes, M.Y. Mohammed, C.J. Pickett, Inorg. Chem. 28 (1989) 3269.
[23] T.A. George, J.R.D. DeBord, B.B. Kaul, C.J. Pickett, D.J. Rose, Inorg. Chem. 31 (1992) 1295.
[24] A.M. Bond, R. Colton, J.J. Jackowski, Inorg. Chem. 14 (1975) 274.
[25] F.L. Wimmer, M.R. Snow, A.M. Bond, Inorg. Chem. 13 (1974) 1617.
[26] J. Jacq, J. Electroanal. Chem. Interfacial Electrochem. 29 (1971) 149.
[27] A. Vallat, M. Person, L. Roullier, E. Laviron, Inorg. Chem. 26 (1987) 332 (and references therein).
[28] (a) D.H. Evans, Chem. Rev. 90 (1990) 739. (b) F. Battaglini, E.J. Calvo, F. Doctorovich, J. Organomet. Chem. 547 (1997) 1.
[29] A.M. Bond, R. Colton, J.B. Cooper, J.C. Traeger, J.N. Walter, D.M. Way, Organometallics 13 (1994) 3434.
[30] A.M. Bond, B.S. Grabaric, J.J. Jackowski, Inorg. Chem. 17 (1978) 2153.
[31] D.A. Cummings, J. McMaster, A.L. Rieger, P.H. Rieger, Organometallics 16 (1997) 4362.
[32] R. Abdel-Hamid, A.A. El-Samahy, M.K.M. Rabia, N. Taylor, B.L. Shaw, Bull. Chem. Soc. Jpn. 67 (1994) 321.
[33] A.M. Bond, R. Colton, D.G. Humphrey, P.J. Mahon, G.A. Snook, V. Tedesco, J.N. Walter, Organometallics 17 (1998) 2977.
[34] A.M. Bond, R. Colton, R.W. Gable, M.F. Mackay, J.N. Walter, Inorg. Chem. 36 (1997) 1181.
[35] K.A. Conner, R.A. Walton, Inorg. Chem. 25 (1986) 4422.
[36] A.M. Bond, R. Colton, J.E. Kevekordes, Inorg. Chem. 25 (1986) 749.
[37] M.F.C. Guedes da Silva, P.B. Hitchcock, D.L. Hughes, K. Marjani, A.J.L. Pombeiro, R.L. Richards, J. Chem. Soc. Dalton Trans. (1997) 3725.
[38] A.M. Bond, R. Colton, S.W. Feldberg, P.J. Mahon, T. Whyte, Organometallics 10 (1991) 3320.
[39] (a) M. Menon, A. Pramanik, N. Bag, A. Chakravorty, J. Chem. Soc. Dalton Trans. (1995) 1543. (b) N. Bag, G.K. Lahiri, A. Chakravorty, J. Chem. Soc. Dalton Trans. (1990) 1557.
[40] A. Pramanik, N. Bag, A. Chakravorty, J. Chem. Soc. Dalton Trans. (1993) 237.
[41] M.A. Bennett, G.A. Heath, D.C.R. Hockless, I. Kovacik, A.C. Willis, J. Am. Chem. Soc. 120 (1998) 932.
[42] F. Létumier, G. Broeker, J.-M. Barbe, R. Guilard, D. Lucas, V. Dahaoui-Gindrey, C. Lecomte, L. Thouin, C. Amatore, J. Chem. Soc. Dalton Trans. (1998) 2233.
[43] T.C. Higgs, D. Ji, R.S. Czernuscewicz, C.J. Carrano, Inorg. Chim. Acta 286 (1999) 80.
[44] G. Barrado, G.A. Carriedo, C. Diaz-Valenzuela, V. Riera, Inorg. Chem. 30 (1991) 4416.
[45] G.A. Carriedo, N.G. Connelly, M.C. Crespo, I.C. Quarmby, V. Riera, G.H. Worth, J. Chem. Soc. Dalton Trans. (1991) 315.
[46] G.A. Carriedo, N.G. Connelly, M.C. Crespo, I.C. Quarmby, V. Riera, J. Chem. Soc. Chem. Commun. (1987) 1806.
[47] M.F.C. Guedes da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, C. Amatore, J.-N. Verpeaux, Organometallics 13 (1994) 3943.
[48] M.F.C. Guedes da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, C. Amatore, J.-N. Verpeaux, Inorg. Chem. 37 (1998) 2344.
[49] M.F.C. Guedes da Silva, C.M.P. Ferreira, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Chem. Soc. Dalton Trans. (1998) 4139.

[50] F.C. Anson, T.J. Collins, S.L. Gipson, J.T. Keech, T.E. Krafft, G.T. Prake, J. Am. Chem. Soc. 108 (1986) 6593.
[51] R.L. Rich, H. Taube, J. Am. Chem. Soc. 76 (1954) 2608.
[52] F. Basolo, R.G. Pearson, Mechanisms of Inorganic Reactions, Wiley, New York, 1967 (and referencess therein).
[53] (a) J.M. Savéant, Acc. Chem. Res. 13 (1980) 323. (b) C. Amatore, J. Pinson, J.M. Savéant, A. Thiebault, J. Electroanal. Chem. Interfacial Electrochem. 107 (1980) 59 (and references therein).
[54] S.W. Feldberg, L. Jeftie, J. Phys. Chem. 76 (1972) 2439 (and references therein).
[55] D. Astruc, Angew. Chem. Int. Ed. Engl. 27 (1988) 643.
[56] (a) K.A. Pevear, M.M.B. Holl, G.B. Carpenter, A.L. Rieger, P.H. Rieger, D.A. Sweigart, Organometallics 14 (1995) 512. (b) B.A. Narayanan, C. Amatore, J.K. Kochi, Organometallics 6 (1987) 129. (c) A. Darchen, H. Mousser, H. Patin, J. Chem. Soc. Chem. Commun. (1988) 968. (d) Also references cited in Refs. [2,45].
[57] C. Amatore, M. Bayachou, J.-N. Verpeaux, L. Pospísil, J. Fiedler, J. Electroanal. Chem. Interfacial Electrochem. 387 (1995) 101.
[58] B.A. Narayanan, C. Amatore, C.P. Casey, J.K. Kochi, J. Am. Chem. Soc. 105 (1983) 6351.
[59] (a) R.D. Rieke, H. Kojima, K. Öfele, J. Am. Chem. Soc. 98 (1976) 6735. (b) R.D. Rieke, H. Kojima, K. Öfele, Angew. Chem. Int. Ed. Engl. 19 (1980) 538.
[60] N.G. Connelly, S.J. Raven, G.A. Carriedo, V. Riera, J. Chem. Soc. Chem. Commun. (1986) 992.
[61] G.M. Acewgoda, B.H. Robinson, J. Simpson, J. Chem. Soc. Chem. Commun. (1982) 284.
[62] W.E. Geiger, in: J.J. Zuckerman (Ed.), Inorganic Reactions and Methods, vol. 15, VCH, New York, 1986 (p. 88).
[63] L.J. Lyons, S.L. Pitz, D.C. Boyd, Inorg. Chem. 34 (1995) 316.
[64] R.N. Bagchi, A.M. Bond, R. Colton, I. Creece, K. McGregor, T. Whyte, Organometallics 10 (1991) 2611.
[65] A.M. Bond, R. Colton, K. McGregor, Inorg. Chem. 25 (1986) 2378.
[66] A. Blagg, S.W. Carr, G.R. Cooper, I.D. Dobson, J.B. Gill, D.C. Goodall, B.L. Shaw, N. Taylor, T. Boddington, J. Chem. Soc. Dalton Trans. (1985) 1213.
[67] A.M. Bond, R. Colton, K. McGregor, Organometallics 9 (1990) 1227.
[68] R.M. Carlos, I.Ap. Carlos, B.S.L. Neto, M.G. Neumann, Inorg. Chim. Acta 299 (2000) 231.
[69] P. Basu, A. Chakravorty, Inorg. Chem. 31 (1992) 4980.
[70] (a) P. Basu, S.B. Choudhury, S. Pal, A. Chakravorty, Inorg. Chem. 28 (1989) 2680. (b) P. Basu, S. Pal, A. Chakravorty, J. Chem. Soc. Chem. Commun. (1989) 977.
[71] D. Ray, A. Chakravorty, Inorg. Chem. 27 (1988) 3292.