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Electron-transfer chain catalysis for the *cis*-to-*trans* isomeric conversion of *cis*-[ReCl(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]

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The low temperature reaction of *cis*-[ReCl(NCC$_6$H$_4$Cl-4)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with CO afforded *cis*-[ReCl(CO)(dppe)$_2$] whose ^{31}P-{^{1}H} NMR spectrum has been analysed as an ABCD spin system. The latter complex in CH$_2$Cl$_2$ slowly converts into the corresponding *trans* isomer (which is oxidised at a higher oxidation potential and whose single crystal X-ray diffraction analysis is also reported) and this isomerisation is promoted by oxidation following an electron-transfer chain (ETC) catalytic process, with low net current flow. This behaviour has been investigated by digital simulation of the cyclic voltammograms at different temperatures and scan rates, which allowed an estimate of the rate constant and the activation parameters for the isomerisation. The relative values of the oxidation potential of the *cis* and *trans* isomers are interpreted on the basis of a metal d$_\pi$ orbital splitting model, the ratio of the isomerisation equilibrium constants (for the pairs of oxidised and parent species) is estimated and the relevance of kinetic factors in the anodically induced isomerisation (which is favoured by the π-electron acceptance ability of the CO ligand) is shown.

Introduction

Since the pioneering work of Rich and Taube,[1] Basolo and Pearson,[2] Saveant and Amatore *et al.*,[3] and Feldberg and Jeftic,[4] electron-transfer-chain (ETC) catalysis is gaining an important role in transition-metal co-ordination chemistry and electrochemistry, and the subject has been reviewed.[5] An ETC catalysed reaction is initiated by electron transfer (ET) but, overall, does not result in a redox change. It is catalysed by the electron or the "electron hole" and the process, in electrochemical terms, can be denoted by $\overrightarrow{E}$ C $\overleftarrow{E}$ ($\overrightarrow{E}$ is the initiation by ET; C is the chemical propagation step; $\overleftarrow{E}$ is the "back ET", the second propagation step which can occur in solution or at the electrode).

A variety of reaction types has been electrocatalysed, mainly including ligand exchange,[6] and, to a smaller extent, *e.g.* ligand insertion[7] or extrusion.[8] Scant examples of complex geometric isomerisation or other structural rearrangements are also known in particular for di- or poly-carbonyl complexes, *e.g.* of molybdenum or tungsten,[9] manganese,[10] cobalt[11] and rhodium.[12]

We now report that the monocarbonyl chloro-complex of rhenium *cis*-[ReCl(CO)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) undergoes an ETC catalysed *cis*-to-*trans* isomerisation to give *trans*-[ReCl(CO)(dppe)$_2$] (whose crystal structure is also included) with the same metal oxidation state, in contrast with the commonly observed anodically induced *cis*-to-*trans* isomerisations of related metal Group 6 dicarbonyl complexes *cis*-[M(CO)$_2$L$_4$] (M = Cr, Mo or W; L = $\frac{1}{2}$ diphosphine)[13] or of the analogous nitrile complexes *cis*-[ReCl(NCR)(dppe)$_2$] (R = C$_6$H$_4$Me-4)[14] or *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$ (R = alkyl or aryl),[15] which yield the isomeric products in an oxidised form, without displaying such an electrocatalytic behaviour.

Moreover, the relative stability of octahedral-type geometrical isomers, the kinetics of their interconversion and the dependence on the electronic count constitute a matter of current interest and considerable debate,[16–29] and generalisations cannot yet be done safely. The rhenium system of this study extends for the first time such an investigation of an ET-induced isomerisation to octahedral 18-/17-electron complexes presenting both a strong π-electron acceptor and an effective π-electron donor ligand (CO and Cl, respectively, whose electronic effects are discussed).

Results and discussion

Synthesis and characterisation of *cis*-[ReCl(CO)(dppe)$_2$] and molecular structure of *trans*-[ReCl(CO)(dppe)$_2$]

The reaction, in CH$_2$Cl$_2$ and at low temperature (see the Experimental section), of CO with *cis*-[ReCl(NCC$_6$H$_4$Cl-4)(dppe)$_2$], a complex which presents the *cis* geometry and a labile nitrile ligand, provides an efficient route for the synthesis of the carbonyl complex with the same geometry, *cis*-[ReCl(CO)(dppe)$_2$], whose isolation and full characterisation is now reported.

Its infrared spectrum shows *ν*(CO) at a value, 1840 cm^{-1} (KBr pellet), that is higher than that we observe, 1795 cm^{-1}, for the known[30,31] *trans* isomer, suggesting that in the *cis* isomer the CO ligand behaves as a weaker π-electron acceptor than when it is in a position *trans* to the strong electron donor Cl$^-$ ligand. In the 550–400 cm^{-1} range (see Experimental section) the former isomer presents only one strong and broad band whereas the latter one exhibits four clearly defined medium intensity bands, in agreement with the previously observed[32] typical isomeric CC stretching vibration patterns of the phenyl rings of the diphosphine ligands.

Moreover, the *cis* geometry of the chlorocarbonyl compound is corroborated by its rather complex ^{31}P-{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 20 °C) which has been analysed as an ABCD spin system (Fig. 1 and Experimental section) by using a LAME iterative program.[33]

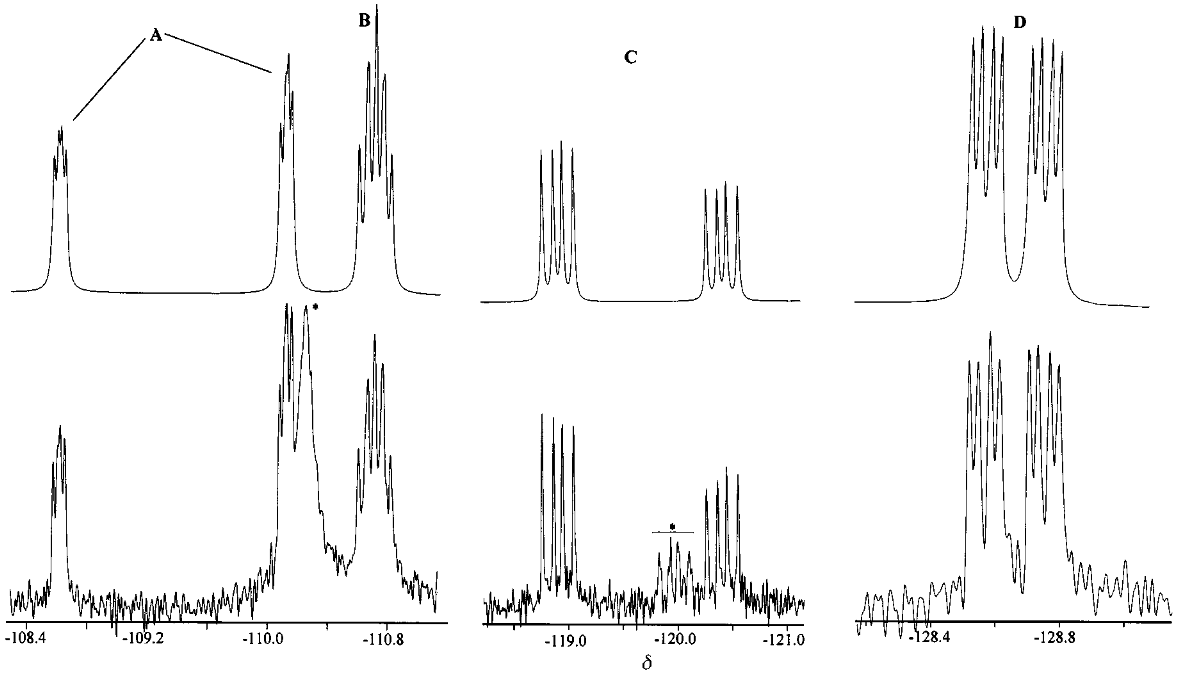


Fig. 1 Theoretical (top) and experimental (bottom) (CD_2Cl_2, 20 °C) $^{31}P\text{-}\{^1H\}$ NMR spectra of *cis*-[ReCl(CO)(dppe)$_2$] analysed as an ABCD spin system (see Experimental section). *Decomposition products.

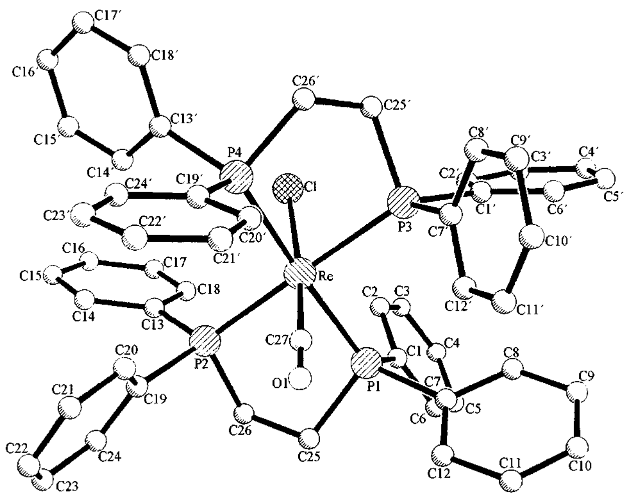


Fig. 2 Molecular structure of *trans*-[ReCl(CO)(dppe)$_2$].

The complex is unstable in dichloromethane solution converting into the thermodynamically favoured *trans* isomer, and this conversion can be monitored by $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectroscopies. However, other decomposition products are also detected, in relative amounts that are temperature dependent, such as *cis*- and *trans*-[Re(CO)$_2$(dppe)$_2$]$^+$ and *trans*-[ReCl$_2$(dppe)$_2$], thus precluding the accurate estimate of the rate constant for the isomerisation process.

The molecular structure of *trans*-[ReCl(CO)(dppe)$_2$] has been determined by single crystal X-ray diffraction analysis and is shown in Fig. 2. Selected bond lengths and angles are listed in Table 1. The Re atom exhibits octahedral co-ordination with the four P atoms in the equatorial positions, whereas the terminal C atom of the carbon monoxide and the chloride occupy the apical positions.

The Re–C distance [1.944(8) Å] is comparable to those observed in other complexes in which a halide is *trans* to the CO ligand, such as *trans*-[ReCl(CO)(dppm)$_2$] (dppm = $Ph_2PCH_2PPh_2$) [1.914(17) and 1.95(3) Å],[34] [ReBr(CO)$_3$(PPh$_3$){C(NHPh)(NHCHMe$_2$)}] [1.940(8) Å],[35] [ReBr(CO)$_4$(PPh$_3$){C(NHPh)(NHCHMe$_2$)}] [1.901(12) Å][35] or [ReCl(CO)$_4$(PPh$_2$H)] [1.895(7) Å].[36] It approaches the value (1.91 Å)[37] estimated for a Re=C double bond, as the sum of the covalent bond radii of Re (1.24 Å) and sp^2 C (0.67 Å), and this observation, combined with the low infrared ν(CO) value (see above), indicates that the CO ligand behaves as an effective π-electron acceptor from the electron-rich rhenium(I) centre. However, the short CO bond distance of 1.003(7) Å is of no diagnostic value.

Table 1 Selected bond lengths (Å) and angles (°) for *trans*-[ReCl(CO)(dppe)$_2$]

Re–C(27)	1.944(8)	Re–P(2)	2.443(2)
Re–P(1)	2.387(2)	Re–Cl	2.542(2)
Re–P(3)	2.417(2)	C(27)–O	1.003(7)
Re–P(2)	2.4307(14)		
C(27)–Re–P(1)	83.0(2)	C(27)–Re–Cl	174.1(2)
C(27)–Re–P(2)	88.5(2)	P(1)–Re–Cl	102.33(5)
C(27)–Re–P(3)	95.6(2)	P(3)–Re–Cl	86.35(5)
C(27)–Re–P(4)	92.3(2)	P(2)–Re–Cl	89.85(5)
Re–C(27)–O	178.4(6)	P(4)–Re–Cl	82.55(5)

In accord with the common oxidation state of the metal, the Re–P bond lengths, in the range 2.387(2)–2.443(2) Å, are comparable with those observed in *trans*-[ReCl(CNR)(dppe)$_2$] [R = Me,[38] average of 2.40 Å; R = Bu^t,[39] 2.382(2)–2.426(2) Å] and in *trans*-[ReCl(NCR)(dppe)$_2$] [R = Me, in the range 2.374(2)–2.420(2) Å].[40] Moreover, and despite the different metal oxidation state, they are also similar to those found in *trans*-[ReCl$_2$(dppe)$_2$] [2.408(2) and 2.424(2) Å][41] in which a shortening of the Re–P distance can result from the π-electron release of the two chloride ligands. However, as expected, they are shorter than those in the oxidised rhenium(III) complex *trans*-[ReCl$_2$(dppe)$_2$]A [A = Cl, 2.4875(4) and 2.5052(4); A = BF$_4$, 2.473(4) and 2.494(4)][41] with a weaker π-electron releaser metal centre.

Electrochemical behaviour of *cis*-[ReCl(CO)(dppe)$_2$]

General. Typical cyclic voltammograms, at different scan rates, for a 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$ solution of *cis*-[ReCl(CO)(dppe)$_2$], at a platinum disc electrode and at

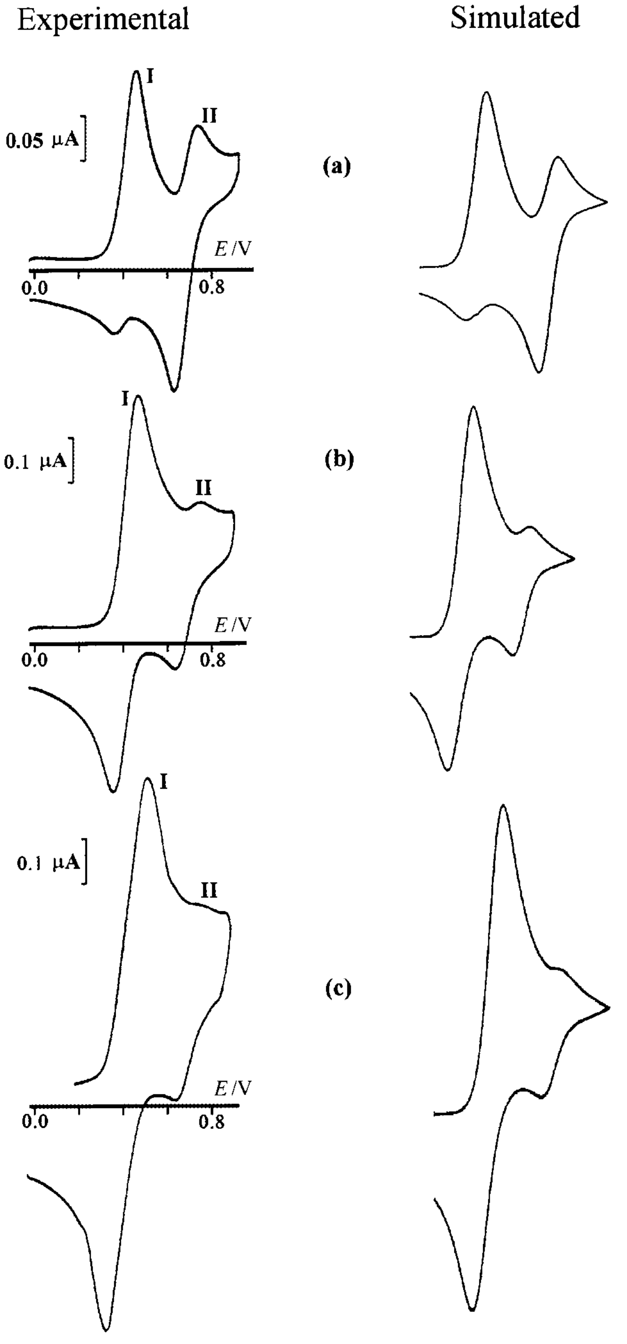


Fig. 3 Experimental (left) and simulated (right) cyclic voltammograms of *cis*-[ReCl(CO)(dppe)$_2$] (0.6 mM, in CH_2Cl_2 with 0.2 M [NBu$_4$][BF$_4$]) at −40 °C and at a platinum-disc ($d = 0.5$ mm) working electrode. Potentials are given in V *vs.* SCE. Scan rate: 0.2 (a), 0.8 (b) and 1.4 V s^{-1}(c).

−40 °C, are shown in Fig. 3 (left hand side). Two waves (I and II) are clearly distinguishable at $E_1° = 0.41$ and $E_2° = 0.68$ V *vs.* SCE, respectively. The reversibility of wave I and its current intensity relative to that of wave II increase with the scan rate towards a single-electron reversible process, with concomitant disappearance of wave II. A similar effect is observed upon lowering the temperature (Fig. 4). These and other observations (see below) indicate that wave II results from the oxidation of a species generated *in situ* upon oxidation, at wave I, of the starting complex, *i.e.* derived from *cis*-[ReCl(CO)dppe)$_2$]$^+$.

Additional evidence for such an overall mechanism is the occurrence of isopotential points[42] (at 0.65 V for the anodic scan, and 0.42 V for the cathodic one, values measured at a scan rate of 1.0 V s^{-1}) observed upon multiple scans cyclic voltammetry (Fig. 5), which indicates that the only transformation observed on the timescale of the experiment is the ET-induced conversion of the starting complex into another one (oxidised at wave II), the sum of their concentrations remaining constant. The presence of the isopotential points also indicates that the same number of electrons is involved in both oxidation processes. After *ca.* 7 scans the cyclic voltammograms achieved a steady state response which would not be obtained if any of the species involved was participating in side reactions during the cyclic voltammetry timescale.

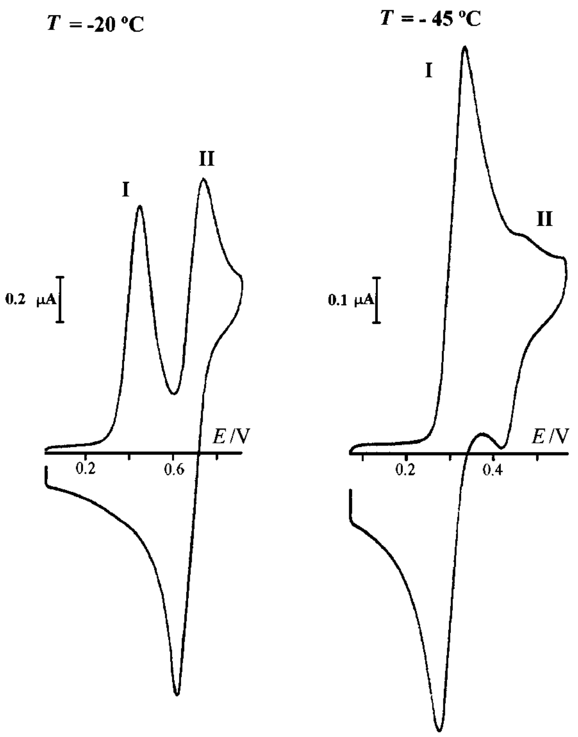


Fig. 4 Effect of temperature in the cyclic voltammogram of *cis*-[ReCl(CO)(dppe)$_2$]. Potentials are given in V *vs.* SCE. Scan rate of 0.8 V s^{-1}.

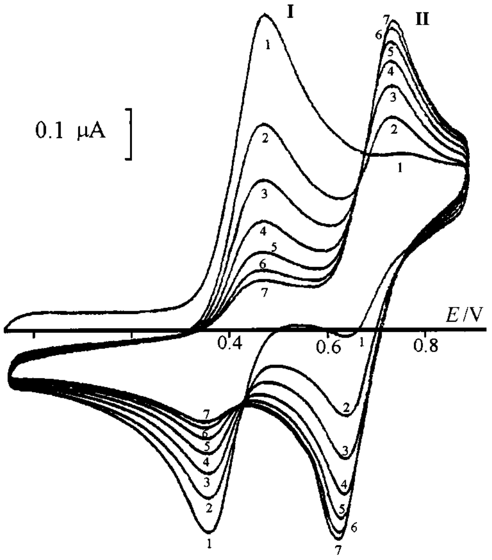
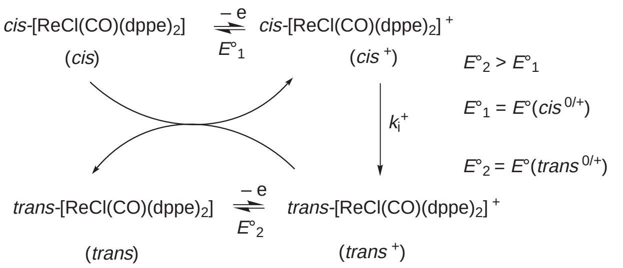


Fig. 5 Multiple scans cyclic voltammetry for 0.6 mM solutions of *cis*-[ReCl(CO)(dppe)$_2$] in CH_2Cl_2 with 0.2 M [NBu$_4$][BF$_4$], at −40 °C. Potentials are given in V *vs.* SCE. Scan rate of 0.2 V s^{-1}.

The product of the oxidation of *cis*-[ReCl(CO)(dppe)$_2$] is the *trans* isomer since the reversible wave II occurs at the same potential as that measured, under identical conditions, for a genuine sample of the latter complex. Moreover, this was confirmed by the identification, by ^{31}P-{^{1}H} NMR, of this isomer [singlet at δ −111.07 relative to P(OMe)$_3$] as the product of the controlled potential electrolysis at the anodic wave I (see below). Hence, the anodic process of the starting *cis* complex involves the *cis*$^+$-to-*trans*$^+$ isomerisation.

However, since $E_2° > E_1°$, *i.e.* $E°$ ($trans^{0/+}$) > $E°$ ($cis^{0/+}$), the *trans*$^+$ product should be reduced by the electrode at the potential ($E_1°$, wave I) at which it is generated to give the reduced *trans* form and the overall process at wave I should therefore involve an electron-transfer chain catalysed (ETC)[1–5] isomerisation ($\vec{E}$ C $\overleftarrow{E}$-type process) according to Scheme 1.



Scheme 1

Moreover, the electrogenerated *trans*$^+$ intermediate should be able to oxidise, in an homogeneous way, the *cis* isomer (cross redox reaction 1), to give *cis*$^+$ and *trans* which thus can also be formed homogeneously once the process is triggered by anodic electron transfer. Therefore, the overall isomerisation is catalytic in electrons whether the electron transfer is heterogeneous or homogeneous.

$$trans^+ + cis \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans + cis^+ \qquad (1)$$

The above ETC catalysis model has been corroborated by controlled potential electrolysis, at −40 °C, of a solution of *cis*-[ReCl(CO)(dppe)$_2$] at a potential slightly above (by *ca.* 50 mV) the anodic peak potential of wave I: the current and charge passed during the coulometry were very small, quite below what would be expected for a one-electron oxidation, and the electrolysis was complete within only a few minutes (after the consumption of less than 0.018 F mol^{-1} corresponding to a coulombic efficiency greater than 56). This low charge was more than enough to burst the catalytic process of conversion of the *cis* into the *trans* isomer since it was sufficient to have a very small amount of *trans*$^+$ in the presence of *cis*.

A cyclic voltammogram of the solution electrolysed at wave I showed only the wave corresponding to the *trans* complex and the current intensity was that expected for a complete *cis*-to-*trans* conversion. The reverse *trans*-to-*cis* isomerisation was not detected either at the level of the cationic or the neutral species.

The oxidation potential of either *cis*- or *trans*-[ReCl(CO)(dppe)$_2$] (0.41 or 0.68 V, respectively) is significantly more anodic than those quoted for the related nitrile or isocyanide complexes *cis*-[ReCl(NCR)(dppe)$_2$] (R = alkyl or aryl, $E°$ = −0.20 to −0.14 V)[43] or *trans*-[ReCl(CNR)(dppe)$_2$] (R = alkyl or *p*-substituted phenyl, $E°$ = 0.06 to 0.30 V)[44] consistent with the expected stronger π-electron acceptor ability of CO compared with NCR or CNR.

A prominent difference between our system and the related ones mentioned above, such as [M(CO)$_2$L$_4$] (M = Cr, Mo or W; L = $\frac{1}{2}$ diphosphine),[13] which undergo a *non*-electrocatalytic anodically induced *cis*-to-*trans* isomerisation, is that the *cis* isomer in our case is oxidised at a lower potential than the *trans* in contrast with the latter systems for which $E°$ ($cis^{0/+}$) > $E°$ ($trans^{0/+}$). This feature of our rhenium system, which confers the ETC catalytic behaviour (see above), can be interpreted qualitatively by considering the expected d$_\pi$ orbital level splitting for d^6 Re in the two isomers (Fig. 6). In fact, the HOMO in the rhenium *cis* isomer is expected to lie at a higher energy than in the *trans*, since the d$_\pi$ orbital in the former isomer that lies in the plane perpendicular to the Re–CO bond and contains the Cl ligand (d$_{xy}$, considering the *z* axis defined by that bond) is destabilised by a filled chlorine d orbital (a π-electron donor), and cannot interact with any of the stabilising empty π* orbitals of CO. In the *trans* isomer the rhenium d$_{xy}$ orbital cannot interact with any of those orbitals, whereas for the d$_{xz}$ and d$_{yz}$ the destabilisation due to the interaction with a filled chlorine d orbital is compensated (at least in part, *i.e.* they can lie either at slightly higher or lower energy than d$_{xy}$) by the stabilising effect due to interaction with a π* orbital of CO (a known strong π-electron acceptor). For the [M(CO)$_2$L$_4$] complexes a different ordering is expected, since for the *cis* isomer all the metal d$_\pi$ orbitals are stabilised by interaction with π*(CO), whereas no stabilisation occurs for d$_{xy}$ of the *trans* isomer which thus lies at a higher energy, *i.e.* $E°$ ($trans^{0/+}$) < $E°$ ($cis^{0/+}$).[19] Therefore, the Cl ligand in our rhenium complexes plays a fundamental role in the reverse of the HOMO energies of the two isomers by destabilising the metal d$_{xy}$ orbital only in the *cis* isomer. Moreover, the model proposed, in a simplified way, in Fig. 6 should be more general, with possible application to other 18-electron octahedral-type complexes with the general formula [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).

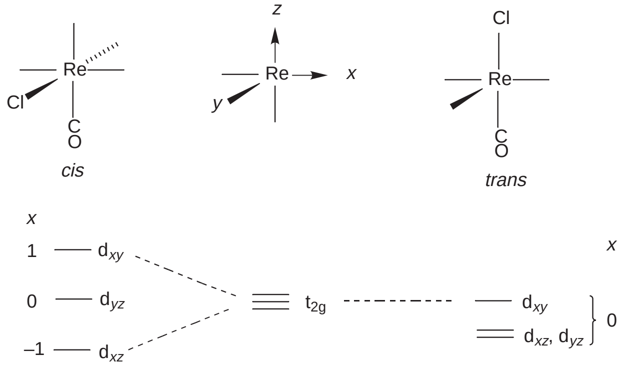
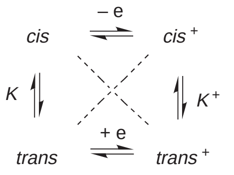


Fig. 6 Proposed qualitative d$_\pi$ orbital level splitting for isomers of [ReCl(CO)L$_4$] (L = $\frac{1}{2}$ diphosphine) [*x* = difference between the number of destabilising interactions with filled chlorine p orbitals and the number of stabilising interactions with empty π* (CO)] (in the *trans* isomer, the relative positions of the d$_{xz}$, d$_{yz}$ and d$_{xy}$ orbitals are shown arbitrarily, see text).

Isomeric equilibria. The reverse in the order of $E°$ for the isomers in our rhenium complex relative to the above mentioned dicarbonyl complexes has an important consequence in terms of differentiating their thermodynamic behaviours. In fact, the isomerisation equilibrium constants and the redox potentials are related by eqn. (2) in which

$$\frac{K^+}{K} = \exp\left\{\frac{F}{RT}[E°(cis^{0/+}) - E°(trans^{0/+})]\right\} \qquad (2)$$

K = [*trans*]/[*cis*] and K^+ = [*trans*$^+$]/[*cis*$^+$], derived from the known $\Delta G° = 0$ condition for the thermochemical cycle of Scheme 2. The ratio K^+/K (eqn. 3) corresponds to the reverse of the equilibrium constant of the cross redox reaction (1).



Scheme 2

$$\frac{K^+}{K} = \frac{[trans^+]}{[cis^+]}\cdot\frac{[cis]}{[trans]} \qquad (3)$$

Hence, since in our rhenium complex $E°$ ($cis^{0/+}$) < $E°$ ($trans^{0/+}$), one concludes that $K^+ < K$ [in fact, $K^+/K = (1.5 \pm 0.7) \times 10^{-6}$], *i.e.* the oxidation does *not* result in a shift of the isomerisation equilibrium towards the *trans* geometry or, in other words, the cross redox equilibrium (1) lies towards the *trans* and cis^+ species rather than the $trans^+$ and *cis* isomers. This situation sharply contrasts with that known for the dicarbonyl complexes.

Therefore, the interpretation of the observed promotion of the *cis*-to-*trans* isomerisation in our rhenium system upon oxidation has to take into consideration the effects of the other reactions (such as the consumption of generated $trans^+$ due to its reduction by the electrode and by *cis*), as well as kinetic factors since the kinetics is expected[13–15] to be much faster at the 17-electron complexes (they can isomerise much quicker) than at the parent 18-electron compounds.

Kinetic data. Digital simulations (CVSim program[45]) of the cyclic voltammograms were used to test the validity of our interpretation and to obtain kinetic data at the oxidised level. The isomerisation at the level of the neutral species is too slow to be detected in the timescale of cyclic voltammetry.

Fig. 3 shows examples of experimental (at −40 °C) and the corresponding simulated (right hand side) cyclic voltammograms for the $\overrightarrow{E}\ C\ \overleftarrow{E}$ mechanism depicted in Scheme 1, by considering the optimised values of the isomerisation rate constant ($k_i^+ = 0.85 \pm 0.15$ s^{-1} at −40 °C) (the rate constants for the other isomerisation processes were taken as insignificant) and of the forward rate constant for the cross redox reaction (1), $k_1 = (9 \pm 2) \times 10^3$ M^{-1} s^{-1} . The value of the corresponding backward rate constant can then be estimated as $k_{-1} = (1.3 \pm 0.9) \times 10^{-2}$ M^{-1} s^{-1} from the knowledge (see above) of the equilibrium constant for this reaction.

The variation of the isomerisation rate constant with the temperature was investigated over the −20 to −50 °C range (Table 2), and the linear log k_i^+ *vs.* 1/*T* Arrhenius plot enabled an estimate of the Eyring and Arrhenius activation parameters: log $A = 13.4 \pm 1.3$, $E_a = 60 \pm 6$ kJ mol^{-1}, $\Delta H^{\neq} = 58 \pm 6$ kJ mol^{-1} and $\Delta S^{\neq} = -4 \pm 20$ J K^{-1} mol^{-1}. A low value for $\Delta S^{\neq}$ could be indicative[13] that the isomerisation would occur *via* an intramolecular twist rather than a dissociative (bond rupture) mechanism, as shown[13] for the above dicarbonyl complexes, but the pronounced uncertainty associated with that value precludes, in our case, a firm conclusion in this respect.

The Arrhenius plot allowed also an estimate of the isomerisation rate constant at 0 °C, and the obtained value ($k_i^+ = 80$ s^{-1}) is higher than that observed at the same temperature (5.6 s^{-1}) for the two-electron induced isomerisation ($cis^{2+} \longrightarrow trans^{2+}$) of the related nitrile complex *cis*-[ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$] which, moreover, even at the monocationic level still isomerises rather slowly (the rate constants relative to the $cis^+/trans^+$ isomerisation equilibrium are much lower than 10^{-4} s^{-1}).[14] These observations indicate that the carbonyl system displays a much higher propensity for isomerisation than the nitrile one, and a conceivable factor for such a higher lability lies in the strong π-electron acceptor character of the carbonyl ligand with a resulting expected labilisation of the Re–P (diphosphine) bonds which can favour the geometrical rearrangement. This is in accord with the observed[15] increase of the rate of the anodically induced isomerisation with the increase of the electron-acceptor character of R in the dinitrile series *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$.

Table 2 Rate constant (k_i^+) for the *cis*-to-*trans* isomerisation of *cis*-[ReCl(CO)(dppe)$_2$]$^+$ at various temperatures

T/°C	k_i^+/s^{-1}
−20	12.5 ± 1.5
−30	2.50 ± 0.45
−35	1.50 ± 0.25
−40	0.85 ± 0.15
−45	0.45 ± 0.10
−50	0.25 ± 0.10

Experimental

All reactions were carried out under dinitrogen, through standard vacuum and inert gas flow techniques. The solvents were dried by standard procedures and freshly distilled before use. The complexes *cis*-[ReCl(NCC$_6$H$_4$Cl-4)(dppe)$_2$][43] and *trans*-[ReCl(N$_2$)(dppe)$_2$][46] were prepared according to published methods. The IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer and NMR spectra on a Varian Unity 300 spectrometer.

The electrochemical experiments were performed on an EG & G PAR 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A) or on an EG & G PAR 173 potentiostat/galvanostat and an EG & G PARC 175 Universal programmer. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum-disc working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum auxiliary electrode was employed. Controlled potential electrolysis was carried out in a two-compartment three-electrode cell with platinum gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver wire pseudo-reference electrode. The electrochemical experiments were performed in an inert atmosphere (N$_2$) both at room temperature and at low temperature. The potentials were measured in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$ and are quoted relative to the saturated calomel electrode (SCE) by using as internal reference the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ couple ($E_{\frac{1}{2}}^{ox} = 0.53$ V *vs.* SCE). The mechanism of the electroinduced isomeric interconversion was investigated by simulation (program CVSIM[45]) of the voltammograms at different scan rates (in the 0.02–50 V s^{-1} range). The $E°$ values were taken as the average of E_{pa} and E_{pc} for both isomers; values for k_{het} for both electron transfers were chosen to give a ΔE_p of 80 mV for the *cis* isomer ($k_{het\text{-}1} = 0.008$ s^{-1}) and 60 mV for the *trans* ($k_{het\text{-}2} = 0.02$ s^{-1}) at a scan rate of 200 mV s^{-1}, in order to allow a close correspondence between simulated and experimental voltammograms.

Synthesis of *cis*- and *trans*-[ReCl(CO)(dppe)$_2$]

The *cis* isomer of the rhenium monocarbonyl compound was synthesized as follows: *cis*-[ReCl(NCC$_6$H$_4$Cl-4)(dppe)$_2$] (0.12 g, 0.10 mmol) was dissolved in dichloromethane (*ca.* 20 cm^3) and the solution was then cooled to −63.5 °C by means of a CHCl$_3$–liquid nitrogen cryogenic bath. Bubbling CO through a glass frit and letting the temperature rise to −15 °C resulted in a change of the solution from red to orange. The solution was immediately cooled to the initial temperature, concentrated *in vacuo* and cold Et$_2$O added, leading to precipitation of the *cis* isomer of [ReCl(CO)(dppe)$_2$] as a yellowish white solid which was filtered off at low temperature, washed with cold Et_2O and dried by passing CO gas through the solid (*ca.* 0.030g, 30% yield). Further crops were contaminated with the *trans* isomer and with unidentified products (Found: C, 58.7; H, 4.6. Calc. for $C_{53}H_{48}ClOP_2Re\cdot0.5CH_2Cl_2$: C, 59.0; H, 4.5%). IR (KBr pellet): 1840s (br) (ν_{co}); 505s (br) cm^{-1} (ν_{cc}, diphosphine). ^1H NMR (CD_2Cl_2): δ 8.14–6.43 (m, 40 H, Ph) and 1.60 (m, 8 H, CH_2). ^{31}P-{^1H} NMR [CD_2Cl_2, relative to $P(OMe)_3$]: δ_A −109.42, δ_B −110.71, δ_C −119.59 and δ_D −128.66 ($J_{AB} = 5.88$, $J_{AC} = 182.98$, $J_{AD} = 3.44$, $J_{BC} = 12.70$, $J_{BD} = 7.61$, $J_{CD} = 22.64$ Hz).

The known complex *trans*-[ReCl(CO)(dppe)$_2$][30,31] can be obtained by different routes, such as the reaction of *trans*-[ReCl(N_2)(dppe)$_2$] with CO or with CO_2 under irradiation,[31] the conversion of *trans*-[Re(CO)$_2$(dppe)$_2$]Cl by heating (270 °C) with dppe in an evacuated tube,[32] or as a side-product in attempted reactions of that dinitrogen complex with other substrates *e.g.* alkynes and guanidine, in thf under reflux or irradiation. The particular sample analysed by single-crystal X-ray diffraction was obtained in a low yield as a side product, upon treatment, in sunlight, of a thf (25 cm^3) solution of *trans*-[ReCl(N_2)(dppe)$_2$] (0.15 g, 0.14 mmol) with guanidine hydrochloride, $H_2NC(=NH)NH_2\cdot HCl$ (0.030 g, 0.31 mmol) in the presence of Tl[BF_4] (0.090 g, 0.32 mmol). After 4.5 h the solution was filtered and taken to dryness *in vacuo*. Extraction with CH_2Cl_2 (10 cm^3), filtration, concentration *in vacuo* and addition of Et_2O led to the precipitation of *trans*-[ReCl(CO)(dppe)$_2$] as a crystalline solid which was filtered off, washed with Et_2O and dried *in vacuo* (*ca.* 0.010 g, 10% yield). IR (KBr pellet): 1825s and 1800m cm^{-1} (ν_{co}); 520ms, 495m, 470m and 420m cm^{-1} (ν_{cc}, diphosphine). ^1H NMR (CD_2Cl_2): δ 7.62–7.02 (m, 40 H, dppe), 2.63 (br, 4 H, CH_2 of dppe) and 2.40 (br, 4 H, CH_2 of dppe). ^{31}P-{^1H} NMR [CD_2Cl_2, relative to $P(OMe)_3$]: δ −111.07 (s).

X-Ray crystallography

Crystal data for *trans*-[ReCl(CO)(dppe)$_2$]·0.5 Et_2O. $C_{55}H_{53}ClO_{1.5}P_4Re$, $M = 1083.50$, monoclinic, space group $C2/c$, $a = 49.112(10)$, $b = 11.068(2)$, $c = 17.965(4)$ Å, $\beta = 100.20(2)°$, $U = 9611(3)$ Å^3, $T = 293(2)$ K, $Z = 8$, μ(Mo-Kα) = 2.758 mm^{-1}. Cell dimensions were obtained from 4576 reflections measured, 4321 independent ($R_{int} = 0.0137$). Final $wR(F^2) = 0.0530$, $R1 = 0.0208$. Intensity data were collected using a Sintex P-1 diffractometer in the range 1.89–22.55° with index ranges $-52 \leqslant h \leqslant 52$, $0 \leqslant k \leqslant 11$, $-19 \leqslant l \leqslant 0$.

CCDC reference number 186/1215.

See http://www.rsc.org/suppdata/dt/1998/4139/ for crystallographic files in .cif format.

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