Electron-Transfer-Induced Geometrical Isomerization of the Dinitrile Complexes *cis*-[Re(NCR)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$] (R = Aryl, Alkyl): Rates, Mechanism, and Ligand Effects

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Received October 10, 1997

In an aprotic medium and at a Pt electrode, *cis*- and *trans*-[Re(NCR)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ (*cis*$^+$ and *trans*$^+$, respectively; R = aryl or alkyl) undergo two successive single-electron oxidations to form the 17-electron (*cis*$^{2+}$ or *trans*$^{2+}$) and 16-electron (*cis*$^{3+}$ or *trans*$^{3+}$) derivatives. The *cis*$^{3+}$ complexes isomerize to the corresponding *trans*$^{3+}$ complexes which undergo a slower decomposition reaction, and the rate constants (k_i^{3+} and k_{dec}, respectively) have been determined by kinetic analysis of the cyclic voltammetric behavior. For the aromatic nitrile complexes, both rate constants increase with the electron-withdrawing ability (Hammett's σ_p constant) of R. The ratios of the isomeric equilibrium constants (*cis*$^{3+}$ ⇄ *trans*$^{3+}$, *cis*$^{2+}$ ⇄ *trans*$^{2+}$, and *cis*$^+$ ⇄ *trans*$^+$), for the aromatic nitrile complexes, also increase with σ_p, the thermodynamic gain in favor of the trans isomer is much higher upon the first oxidation than upon the second one, and it decreases with the increase of σ_p (higher sensitivity of the energy of the HOMO of the trans isomers to the electronic effect of R). For the alkyl cyanide complexes, steric effects play a dominant role on their thermodynamic and kinetic behaviors, by shifting anodically the oxidation potential and enhancing the isomerization rate. The significance of those systems in terms of developing a "molecular hysteresis" behavior is also discussed.

Introduction

Structural changes of coordination compounds induced by electron-transfer constitute a matter of current and growing interest.[1−3] The chemical step is often induced by a single-electron-transfer, but in those systems for which no reaction is observed, one should also consider the effect of a second electron-transfer, a subject that has commonly not yet been quantitatively explored.[4,5]

The relative stability and the oxidation potential of octahedral-type geometrical isomers depend on their electronic count,[6−20] although steric factors[18] and the electron donor/acceptor character of the ligands[20] and the metal[18] also play a significant

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(1) (a) Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351. (b) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275.

(2) Astruc, D. *Electron Transfer and Radical Processes in Transition-Metal Chemistry*; VCH Publishers: New York, 1995.

(3) Pombeiro, A. J. L., McCleverty, J., Eds.; *Molecular Electrochemistry in Inorganic, Bioinorganic and Organometallic Compounds*; NATO ASI Series; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993.

(4) (a) Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063. (b) Quarmby, I. C.; Geiger, W. E. *Organometallics* **1992**, *11*, 436. (c) Edwin, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 7104. (d) Geiger, W. E.; Salze, A.; Edwin, J.; Philipsborn, W.; Piantini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113. (e) Geiger, W. E.; Edwin, J. *J. Am. Chem. Soc.* **1987**, *109*, 7893.

(5) Darchen, A.; Mousser, H.; Patin, H. *J. Chem. Soc., Chem. Commun.* **1988**, 968.

(6) Dubois, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1977**, *1*, 479.

(7) Murrell, J. N.; Al-Derzi, A.; Leigh, G. J.; Guest, M. F. *J. Chem. Soc., Dalton Trans.* **1980**, 1425.

(8) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

(9) Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299.

(10) Vallat, A.; Person, M., Roullier, L.; Laviron, E. *Inorg. Chem.* **1987**, *26*, 332; and refs. therein.

(11) (a) Bond, A. M.; Colton, R.; Cooper, J. B.; Traeger, J. C.; Walter, J. N.; Way, D. M. *Organometallics* **1994**, *13*, 3434. (b) Bond, A. M.; Colton, R.; Kevekords, J. E. *Inorg. Chem.* **1986**, *25*, 749. (c) Bond, A. M.; Grabaric, B. S.; Jackowski, J. J. *Inorg. Chem.* **1978**, *17*, 2153. (d) Bond, A. M.; Cotton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 274. (e) Nimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

(12) (a) Bagchi, R. N.; Bond, A. M.; Colton, R.; Greece, I.; McGregor, K.; Whyte, T. *Organometallics* **1991**, *10*, 2611. (b) Bond, A. M.; Colton, R.; Feldberg, S. W.; Mahon, P. J.; White, T. *Organometallics* **1991**, *10*, 3320.

(13) Conner, K. A.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 4422.

(14) Barrado, G.; Carriedo, G. A.; Diaz-Valenzuela, C.; Piera, V. *Inorg. Chem.* **1991**, *30*, 4416.

(15) Blagg, A.; Carr, S. W.; Cooper, G. R.; Dobson, I. D.; Gill, J. B.; Goodall, D. C.; Shaw, B. L.; Taylor, N.; Boddington, T. *J. Chem. Soc., Dalton Trans.* **1985**, 1213.

(16) Lyons, L. J.; Pita, S. L.; Boyd, D. C. *Inorg. Chem.* **1995**, *34*, 316.

(17) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Amatore, C.; Verpeaux, J.-N. *Organometallics* **1994**, *13*, 3943.

(18) (a) Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1543. (b) Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1993**, 237 (c) Bag, N.; Lahiri, G. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1990**, 1557.

(19) (a) Basu, P.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 4980. (b) Basu, P.; Choudhury, S. B.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1989**, *28*, 2680.

(20) Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.* **1986**, *108*, 6593.

S0020-1669(97)01257-3 CCC: $15.00

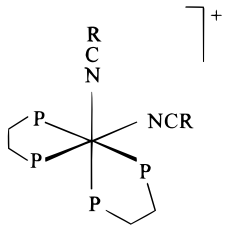
Table 1. Cyclic Voltammetric[a] and Kinetic[b] Data for Complexes *trans*- and *cis*-$[Re(NCR)_2(dppe)_2]^+$

	trans isomers			cis isomers		
R	$E°(trans^{+/2+})$	$E°(trans^{2+/3+})$	k_{dec}/s^{-1}	$E°(cis^{+/2+})$	$E°(cis^{2+/3+})^c$	$k_i^{3+} \times 10^{-2}/s^{-1}$
$C_6H_4NEt_2$-4[d]	0.11	0.99		0.29	1.09	0.40 ± 0.02
C_6H_4OH-4	0.27	1.35		0.40	1.37	7.5 ± 2
C_6H_4OMe-4	0.31	1.33	0.25 ± 0.08	0.44	1.37	10 ± 1
C_6H_4Me-4	0.36	1.41	0.75 ± 0.06	0.49	1.43	15 ± 2
Ph	0.40	1.42		0.52	1.47	*e*
C_6H_4F-4	0.42	1.46	1.5 ± 0.6	0.51	1.47	20 ± 3
C_6H_4Cl-4	0.46	1.47	1.8 ± 0.4	0.55	1.52	25 ± 1
^iPr	0.29	1.41		0.42	1.46	13 ± 2
^tBu	0.33	1.44		0.47	1.46	10 ± 1
Me	0.22	1.34		0.36	1.43	*f*
$CH_2C_6H_4Cl$-4	0.13			0.40	1.46	*f*

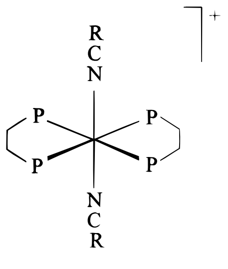
[a] Values in V ± 0.01 relative to SCE, measured at a Pt disc electrode ($\phi = 0.5$ mm), in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$, by using as internal reference the *trans*-$[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ couple ($E° = 0.53$ V vs SCE); scan rate, 0.2 V s^{-1}. [b] The rate constant (k_{dec}) for the decomposition process of $trans^{3+}$ was determined by using the CVSIM simulation program (ref 22); the rate constant (k_i^{3+}) for the cis-to-trans isomerization process of cis^{3+} was determined by using our previously reported (ref 15) CV simulation program; the standard deviation values are also indicated. [c] For those compounds whose $E°(cis^{2+/3+})$ values could not be measured due to a fast isomerization process, the values listed were obtained by considering a peak-to-peak separation of the $cis^{2+/3+}$ wave identical to that observed for the $trans^{2+/3+}$ one and were confirmed by CV simulation. [d] Irreversible anodic wave at 1.34 V due to the oxidation of the amine group. [e] Too low to be measured with acceptable accuracy. [f] Value not estimated because the trans isomer has not been isolated in a pure form, without contamination by the cis one.

role. Some theoretical calculations[6−8] and semiempirical predictions have been reported,[9] and such behavior can be of significance in bioinorganic processes.[21] Attempts for systematic investigations of such factors are scarse, although the effects of the chelating phosphine or amine ligands[12,15] and of the ligand substituent[20] on the electrochemical behaviors of the isomers have been reported.

Most of the studies have been performed on single-electron-transfer processes of carbonyl complexes.[8−16] Conflicting situations have been recognized even for closely related complexes.[22] Therefore, the investigation should be extended to systems presenting a variety of ligands with different electronic and stereochemical properties, as well as to processes which require the transfer of more than one electron, and some of our complexes with nitrogenase substrates[23] appear to be particular promising. We have already reported[17] that the chloro−nitrile complex *cis*-$[ReCl(NCC_6H_4Me\text{-}4)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) is oxidized via two successive single-electron-transfers to form sequentially the corresponding 17-electron (cis^+) and 16-electron (cis^{2+}) complexes, the latter undergoing a facile isomerization to its trans isomer. That rhenium complex possesses a moderate π electron acceptor (NCR) and a strong electron donor (Cl). This study is now extended to a type of systems possessing two moderate π electron acceptor ligands, viz. the series of dinitrile complexes *cis*- and *trans*-$[Re(NCR)_2(dppe)_2]^+$ [denoted by cis^+ and $trans^+$, respectively; R = C_6H_4X-4 (X = NEt_2, OH, OMe, Me, H, F, Cl), Bu^t, Pr^i, Me, $CH_2C_6H_4Cl$-4]. We observed the occurrence of an oxidative overall two-electron-transfer-induced cis to trans isomerization ($cis^{3+} \rightarrow trans^{3+}$) apart from a slower degradation of the $trans^{3+}$ species. The kinetics and thermodynamics [for the $cis^{n+}/trans^{n+}$ (n = 1−3) equilibria] respond to electronic effects for the aromatic nitrile complexes, although steric factors appear to play an important role in the case of the alkylnitrile compounds.

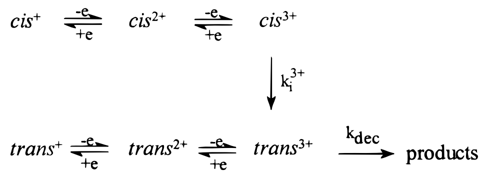


cis^+



$trans^+$

Scheme 1



Results and Discussion

General Anodic Behavior of trans and cis Isomers of $[Re(NCR)_2(dppe)_2]^+$. In cyclic voltammetry (CV) at a Pt electrode, in 0.2 M $[NBu_4][BF_4]/CH_2Cl_2$, at $\nu > 2$ V s^{-1}, each of the trans isomers of $[Re(NCR)_2(dppe)_2]^+$ (denoted by $trans^+$) undergoes two consecutive and reversible single-electron oxidation waves (Table 1).

Controlled potential electrolysis (CPE) on the plateau of the first wave consumes 1 faraday/mol to form the corresponding stable $trans^{2+}$ complex which, upon cathodic CPE, regenerates the parent $trans^+$ compound. However, CPE at the second wave of $trans^+$ (2 faradays/mol) does not afford $trans^{3+}$ as the stable product. In agreement, in cyclic voltammetry of $trans^+$ at slow scan rate ($\nu < 0.2$ V s^{-1}), the second anodic wave has a chemically irreversible character (Figure 1a), although the first one remains fully reversible. Hence the anodic behavior of the *trans* isomers is described by the lower reaction sequence of

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(21) Eady, R. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1994**, 2739.

(22) (a) George, T. A.; Debord, J. R. D.; Kaul, B. B.; Pickett, C. J.; Rose, D. J. *Inorg. Chem.* **1992**, *31*, 1295. (b) George, T. A.; Hayes, R. K.; Mohammed, M. Y.; Pickett, C. J. *Inorg. Chem.* **1989**, *28*, 3269.

(23) For reviews, see: (a) Pombeiro, A. J. L. In *Molecular Electrochemistry in Inorganic, Bioinorganic and Organometallic Compounds*; NATO ASI Series; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993; p 331. (b) Pombeiro, A. J. L. In *Transition Metal Carbyne Complexes*; Kreissl, F. R., Ed.; NATO ASI Series, Kluwer Academic Publishers; Dordrecht, 1993; p 105. (c) Pombeiro, A. J. L. *New J. Chem.* **1994**, *18*, 163. (d) Pombeiro, A. J. L. *Inorg. Chim. Acta* **1992**, *198−200*, 179. (e) Pombeiro, A. J. L.; Richards, R. L. *Coord. Chem. Rev.* **1990**, *104*, 13.

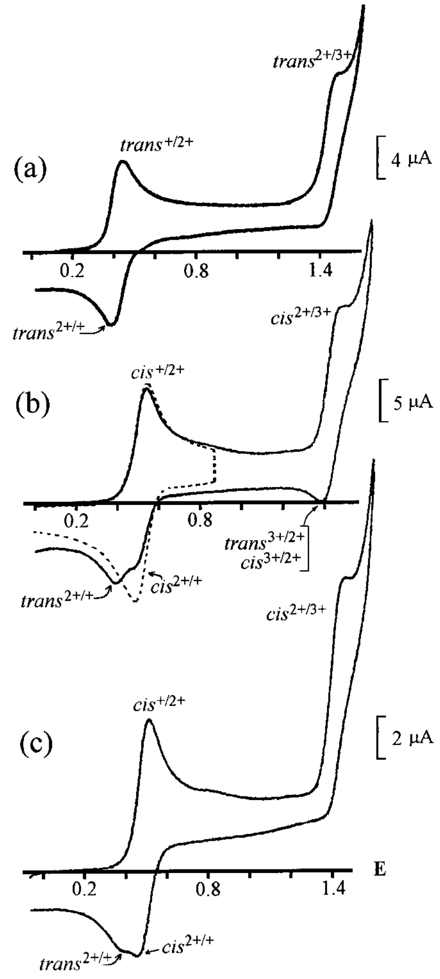

Figure 1. Cyclic voltammograms for [Re(NCC$_6$H$_4$F-4)$_2$(dppe)$_2$][BF$_4$] in 0.2 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ at 25 °C and at a platinum disc electrode ($\phi = 0.5$ mm): trans isomer (0.3 mM) at $\nu = 0.2$ V s^{-1} (a); cis isomer (0.6 mM) at $\nu = 0.2$ V s^{-1} (b) including a hold of potential (20 s) on the plateau of the first wave (- - -), and at $\nu = 0.05$ V s^{-1} (c). Potentials in Volt vs SCE.

Scheme 1 in which the *trans*$^+$, *trans*$^{2+}$, and *trans*$^{3+}$ are 18-, 17-, and 16-electron complexes of Re(I), Re(II), and Re(III), respectively, and the chemical reaction of *trans*$^{3+}$ leads to a nontractable product.

The electrochemical behavior of cis isomers differs greatly. Their cyclic voltammetry also shows two successive one-electron anodic waves. The first one is chemically reversible with $E°$(*cis*$^{+/2+}$) significantly higher (by ca. 0.09−0.27 V) than those observed for the corresponding *trans*$^{+/2+}$ process. This complies with semiempirical predictions[9] for the isomers of 18-electron complexes of the type [ML$_2$L′$_4$] in which L is a better π electron acceptor ligand than L′.

When the second oxidation wave is scanned, a complicated cathodic pattern is observed. The origin of this complication is clearly detected at the Re(II/I) level, with the appearance of the corresponding *trans*$^{2+/+}$ cathodic wave in addition to that of *cis*$^{2+/+}$ (Figure 1b,c). The former occurs with a relative current intensity increasing with a decrease of scan rate although only up to a maximum value, after which a lowering is observed (see below). The cathodic *trans*$^{3+/2+}$ wave is also detected although overlapping with that of *cis*$^{3+/2+}$. This is clearly seen for the C$_6$H$_4$NEt$_2$-4 complex, for which $E°$(*cis*$^{2+/3+}$) and $E°$(*trans*$^{2+/3+}$) differ significantly (Figure 2). The waves of the trans isomer are detected in the voltammetry of the cis isomer only upon formation of *cis*$^{3+}$ (Figure 1b).

Kinetic Investigation of the Anodically Induced Isomerization and Decomposition Processes. Due to the very close proximity of the redox potentials of the second oxidation waves for the cis and trans isomers, and their location near the wall of oxidation of the electrolyte medium, accurate measurements of current intensities are only possible for the well-separated cathodic Re(II) → Re(I) waves.

The determination of the *cis*$^{3+}$ → *trans*$^{3+}$ isomerization rate ($k_i{}^{3+}$) requires the knowledge of the amount of *trans*$^{3+}$ formed by this reaction as a function of time (scan rate). This could be monitored, although indirectly, by measuring the amount of *trans*$^{2+}$ being reduced at the *trans*$^{2+/+}$ cathodic wave, i.e. by plotting $\rho = i_p(trans^{2+/+})/i_p(cis^{+/2+})$ as a function of the scan rate. Such a plot contains the required kinetic information, but two other independent phenomena superimpose: (i) the diffusion during the reverse scan between the tricationic and the dicationic sets of reduction waves which are separated by a large potential difference (ca. 1.0 V) and (ii) the decomposition of *trans*$^{3+}$.

The former effect leads to an apparent lowering of the extent of isomerization, as measured by ρ, because of the diffusional removal from the vicinity of the electrode of the *trans*$^{3+}$ and *trans*$^{2+}$ species, with a concomitant compensation of the reactant

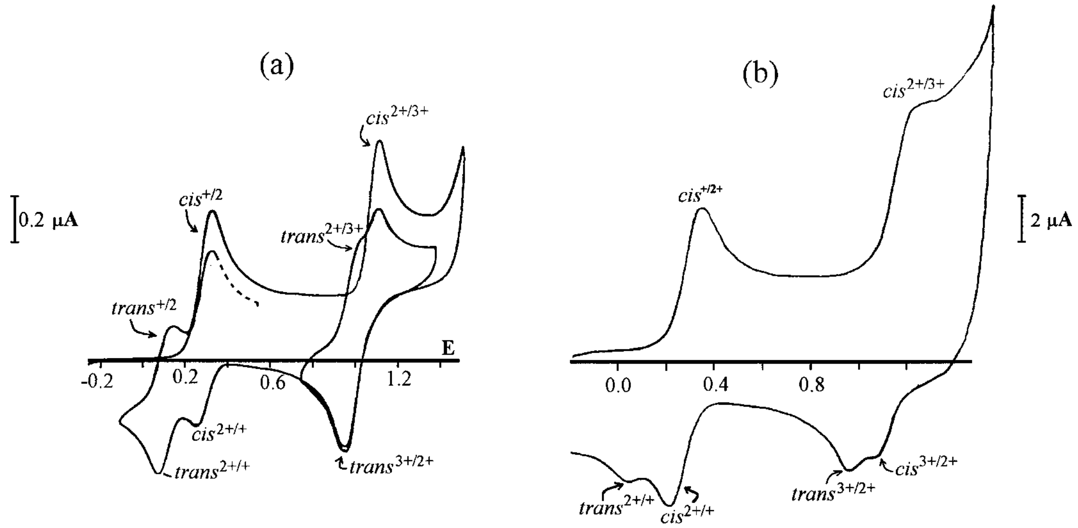

Figure 2. Cyclic voltammograms for *cis*-[Re(NCC$_6$H$_4$NEt$_2$-4)$_2$(dppe)$_2$][BF$_4$] (1.1 mM) in 0.2 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ at 25 °C and at a platinum disc electrode ($\phi = 0.5$ mm) at $\nu = 0.2$ V s^{-1} (a) and 20 V s^{-1} (b). Potentials in volts vs SCE.

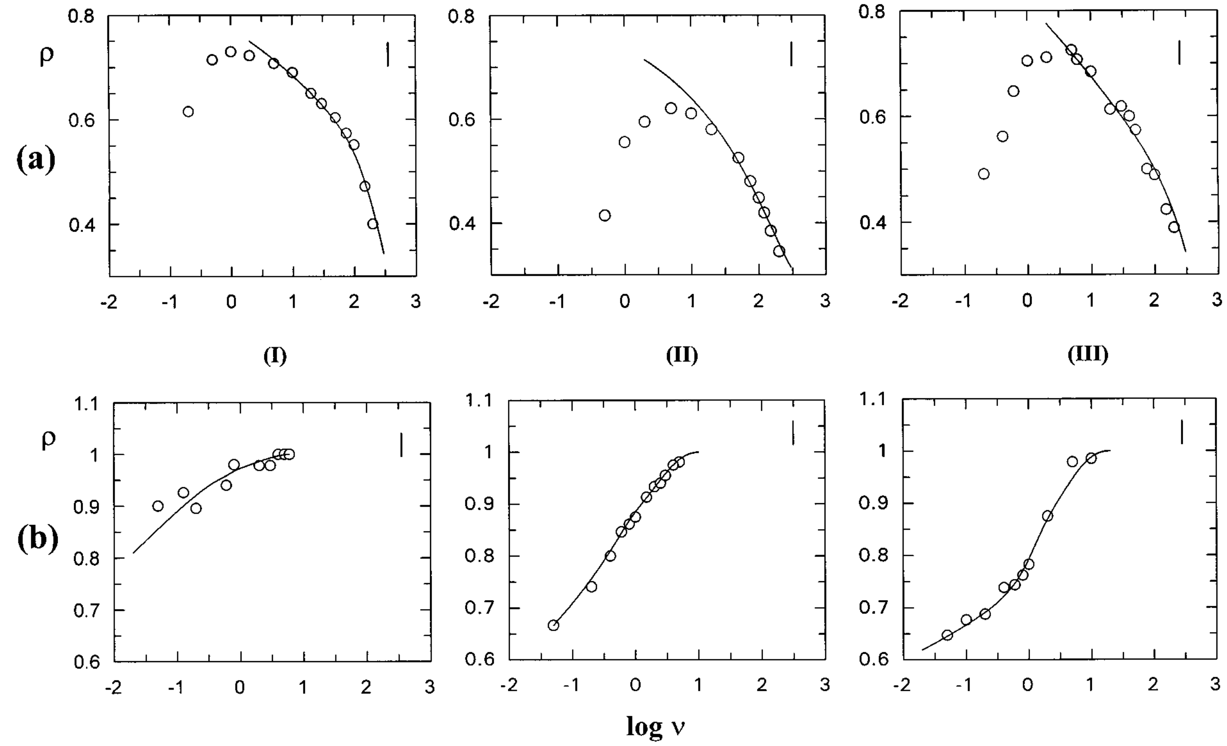

Figure 3. Experimental (○) and theoretical (—) variations of the current ratio ρ as a function of scan rate for the cis [(a), $\rho = i_p(trans^{2+/+})/i_p(cis^{+/2+})$] and trans [(b), $\rho = i_p(trans^{2+/+})/i_p(trans^{+/2+})$] isomers of $[Re(NCR)_2(dppe)_2]^+$ [R = C_6H_4OMe-4 (I), C_6H_4Me-4 (II), C_6H_4F-4 (III)]. Experimental error bars are shown at the top right corner.

cis^+ by diffusion from the bulk of solution toward the electrode surface where it rapidly oxidizes to cis^{2+}; this accounts, e.g., for the observation (Figure 2a) of the cathodic $cis^{2+/+}$ wave even when the $cis^{3+} \rightarrow trans^{3+}$ isomerization is complete at the level of the anodic $cis^{2+/3+}$ wave. This effect (i) should not depend on the scan rate but only on the extension of the potential scan.

The second effect (ii) is expected to be dependent on the scan rate, being neglectable at sufficiently high scan rates (when the decomposition does not occur significantly), but with an increasing significance for lower scan rates, with a resulting decrease of the $trans^{2+}$ (formed upon reduction of $trans^{3+}$) reduction wave.

The combination of these effects with the anodically induced $cis^{3+} \rightarrow trans^{3+}$ isomerization accounts qualitatively for the bell-shaped plot of ρ vs log v (Figure 3a). The rising part of the plot, upon decreasing the scan rate (right-hand side of Figure 3a), corresponds to an increase of the extent of the $cis^{3+} \rightarrow trans^{3+}$ isomerization provided v remains sufficiently fast to prevent any appreciable $trans^{3+}$ decomposition. The decay of ρ, upon decreasing the scan rate on the left-hand side of Figure 3a, corresponds to an increasing extent of such a decomposition, while the isomerization is nearly complete.

The rate of decomposition of $trans^{3+}$ could be obtained by simulation (CVSIM[24]) of the cyclic voltammetric behavior of pure $trans^+$. Both the experimental and the simulated plots of $i_p(trans^{2+/+})/i_p(trans^{+/2+})$ vs scan rate are depicted in Figure 3b; a perfect agreement is obtained between these plots, and the corresponding values for k_{dec} (pseudo-first-order rate constant) are given in Table 1.

These plots also allow us to determine the rate constant limit (usually log ν is ca. 0.5–1.0) above which the $trans^{3+}$ decomposition process does not occur significantly [$i_p(trans^{2+/+})/i_p(trans^{+/2+}) \approx 1$].[25,26] Above that limiting value, the $cis^{3+} \rightarrow trans^{3+}$ isomerization process occurs without interference of the decomposition reaction. The intensity of the reduction wave of $trans^{2+}$ electrochemically generated from the cis isomer then depends only on the isomerization reaction and diffusional effects as observed[17] with $[ReCl(NCC_6H_4Me\text{-}4)(dppe)_2]$, although without significant occurrence of the backward $trans^{3+} \rightarrow cis^{3+}$ isomerization. The $cis^{3+} \rightarrow trans^{3+}$ isomerization rate constant (k_i^{3+}) was determined similarly.

In the particular case of $[Re(NCC_6H_4NEt_2\text{-}4)_2(dppe)_2]^+$, for which k_{dec} for the $trans^{3+}$ isomer was too low to be determined, the backward isomerization process (k_{-i}^{3+}) could take place, leading to $k_{-i}^{3+}/k_i^{3+} = 0.025 \pm 0.003$ with $k_i^{3+} = 40 \pm 2$ s^{-1} and $k_{-i}^{3+} = 1.0 \pm 0.2$ s^{-1}.

The working curves thus obtained (see Figure 3a), based on

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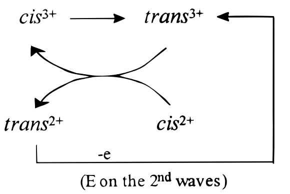
[24] Gosser, D. K.; Zhang, F. *Talanta* **1991**, *38*, 715.

[25] Nevertheless, the descending part of the bell-shaped curve of $i_p(trans^{2+/+})/i_p(cis^{+/2+})$ at decreasing scan rates (left-hand side of Figure 3a) falls more abruptly than the corresponding part of $i_p(trans^{2+/+})/i_p(trans^{+/2+})$ for a solution of the pure trans isomer (Figure 3b), because (i) in the latter case diffusion of this isomer from the bulk of the solution to the electrode surface results in an enhancement of $i_p(trans^{2+/+})$, and (ii) when starting from the cis^+ the decomposition of $trans^{3+}$ hampers the autocatalytic formation of this species (upon reaction with cis^{2+}) while the potential spans over the second waves, with a resulting decrease of its overall generated amount (a type of process which has been discussed earlier in detail in other systems; see ref 26):



[26] Amatore, C.; Pinson, J.; Saveánt, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930.

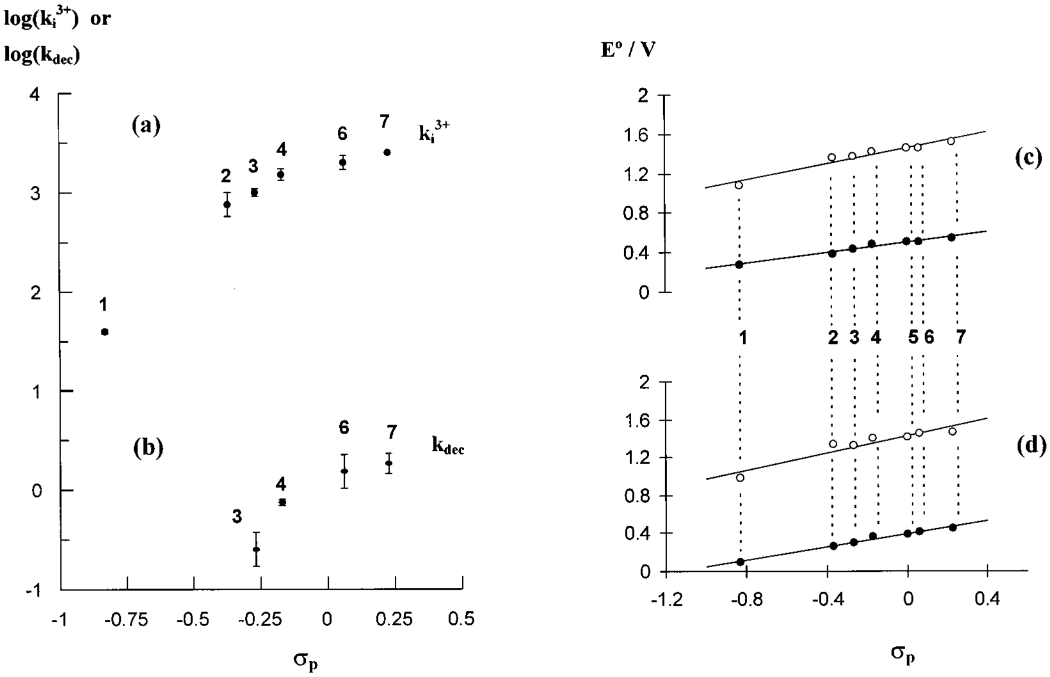


Figure 4. Plots of the rate constant for the isomerization process of *cis*$^{3+}$ (log k_i^{3+}) (a), of the rate constant for the decomposition process of *trans*$^{3+}$ (log k_{dec}) (b), of $E°$ (V ± 0.01 vs SCE) for the first (●) and second (○) anodic waves of *cis*- (c) and *trans*-[Re(NCR)$_2$(dppe)$_2$]$^+$ (d) (R = aryl), vs Hammett's σ_p constant [for the phenyl substituent of the aromatic NCR ligands; R = $C_6H_4NEt_2$-4 (1), C_6H_4OH-4 (2), C_6H_4OMe-4 (3), C_6H_4Me (4), C_6H_5 (5), C_6H_4F-4 (6), C_6H_4Cl-4 (7)].

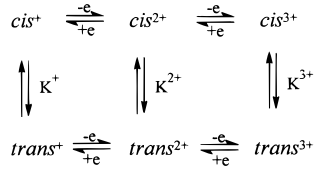
Scheme 1 and on the pertinent series of homogeneous electron transfers fit quite well the experimental data in the above mentioned range of scan rates. The values of k_i^{3+} ((25−0.4) × 10^2) (Table 1) are higher than that measured (5.6 s^{-1})[17] for *cis*-[ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$]$^{2+}$ which presents a more electron-rich metal center.

For the aromatic dinitrile complexes both the isomerization and the degradation rate constants increase with the electron withdrawing ability of the phenyl substituent, as indicated by the plots of log k_i^{3+} or log k_{dec}, respectively, vs the Hammett's σ_p constant (Figure 4a and b). Hence, the geometrical rearrangement of the *cis*$^{3+}$ molecule, which is believed to occur via an intramolecular twist mechanism (as reported[10,11] for other cases), is promoted by a decrease of the electron release from the nitrile ligands to the metal with a conceivable concomitant weakening of the metal−nitrile and metal−phosphine ligand bonds. Similarly, for the alkyldinitrile complexes, k_i^{3+} increases (although the variation is close to the limit of the experimental error) from Bu^t to Pr^i . However, the alkyl dinitrile complexes do not isomerize at slower rates than the aromatic ones conceivably because of steric effects which have a significant role in the case of the former complexes. In fact, such a type of effects is expected to favor the trans geometry, mainly at relatively high metal oxidation states, such as Re(III), when π electronic effects are hampered, thus providing a further driving force for the cis-to-trans isomerization.

The promotion of the rate of decomposition of *trans*$^{3+}$ upon increasing the electron withdrawing character of the R group suggests that the decomposition process involves a nucleophilic addition to the nitrile ligands or to the metal.[2,3,27]

Correlations between kinetic and electronic constants have been reported[28] for the hydride−isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$]$^+$ which, upon anodic oxidation, undergo metal−hydride bond cleavage with proton loss; the rate constant of this cleavage correlates with the net electron donor/acceptor character of the trans isocyanide ligand.

Scheme 2



Because the solutions of *cis*$^{2+}$ or *trans*$^{2+}$ isomers, generated by CPE from the *cis*$^+$ or *trans*$^+$ precursors, are stable on this time scale (at least 30 min), the rate constants, k_i^{2+} and k_{-i}^{2+}, relative to the *cis*$^{2+}$/*trans*$^{2+}$ isomerization (K^{2+} equilibrium in Scheme 2) are much lower than 10^{-4} s^{-1}.

Relative Stability of the cis/trans Isomeric Pairs. Thermodynamic Study. The aromatic *cis*$^+$ isomers of Re(I) isomerize quantitatively to the corresponding *trans*$^+$ complexes by a prolonged heating. This indicates that, even at this low redox level, trans isomers are thermodynamically more stable, a situation that differs from that commonly observed for other 18-electron complexes with an electron-richer metal binding center, such as [ReCl(NCC$_6$H$_4$Me-4)(dppe)$_2$],[17] and [M(CO)$_2$(LL)$_2$] (M = Cr, Mo, W; LL = diphosphine).[10,11] In these complexes, the nitrile or the carbonyl ligands are strong π electron acceptors and the cis isomer is thermodynamically more stable than the trans one. In our cationic dinitrile complexes, the nitrile ligands are expected to be weaker π electron acceptors leading to an inversion of the relative isomeric stability as complexes presenting two π electron donor ligands.[8]

In our electrochemical study we did not detect any isomeric interconversion either at the Re(I) or the Re(II) oxidation state

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(27) (a)Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1988. (c) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(28) Lemos, M. A. N. D. A.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1992**, *438*, 158.

Table 2. Equilibrium Constants for the Homogeneous Electron-transfer Reactions[a]

R	K^{2+}/K^{+}	K^{3+}/K^{2+}	K^{3+}/K^{+}
$C_6H_4NEt_2$-4	1.1×10^3	49.2	5.4×10^4
C_6H_4OH-4	1.6×10^2	2.2	3.5×10^2
C_6H_4OMe-4	1.6×10^2	4.8	7.7×10^2
C_6H_4Me-4	1.6×10^2	2.2	3.5×10^2
Ph	1.1×10^2	7.0	5.4×10^4
C_6H_4F-4	3.3×10	1.5	4.9×10
C_6H_4Cl-4	3.3×10	7.0	2.3×10^2
^{i}Pr	1.6×10^2	7.0	1.1×10^3
^{t}Bu	2.3×10^2	2.2	5.1×10^2
Me	2.3×10^2	33.4	7.7×10^3
$CH_2C_6H_4Cl$-4	3.7×10^4		

[a] See eqs 1−3 in the text.

level, due to the slow kinetics of the processes. At the Re(III) level, a much faster $cis^{3+} \rightarrow trans^{3+}$ isomerization was observed and its rate constant (k_i^{3+}) was determined, but not that for the backward isomerization (except for R = $C_6H_4NEt_2$-4). This prevented the estimate of the corresponding $cis^{3+} \rightleftarrows trans^{3+}$ equilibrium constant ($K^{3+} = [trans^{3+}]/[cis^{3+}]$). However, by taking into consideration that the isomerization $trans^{3+} \rightarrow cis^{3+}$ is necessarily slower[27] than the decomposition reaction of $trans^{3+}$ a lower limit for K^{3+} can be obtained. Thus, $K^{3+} \gg k_i^{3+}/k_{dec}$, i.e. greater than 4×10^3, 2×10^3, 1.3×10^3, or 1.4×10^3 for the pairs of isomers with the NCC_6H_4X-4 ligands (X = OMe, Me, F, or Cl, respectively). Hence, the equilibrium at the Re(III) level lies well in favor of the trans isomer ($K^{3+} \gg 10^3$, in every case).

It was also possible (see Experimental Section) to compare the relative isomeric stabilities at the various redox states, i.e. to obtain the ratios K^{2+}/K^{+}, K^{3+}/K^{2+}, and K^{3+}/K^{+} of the equilibrium constants $K^{+}(cis^{+} \rightleftarrows trans^{+})$, $K^{2+}(cis^{2+} \rightleftarrows trans^{2+})$, and $K^{3+}(cis^{3+} \rightleftarrows trans^{3+})$ of the homogeneous electron-transfer cross-reactions 1−3, respectively (Table 2). A significant thermodynamic gain is observed toward the formation of the trans isomer upon either the first-electron oxidation (K^{2+}/K^{+} in the range from 33 to 1.1×10^3 for the aromatic nitrile complexes) or, to a lower extent, the second-electron removal (K^{3+}/K^{2+} in the range from 1.5 to 49.2); the overall effect is also expressed by the K^{3+}/K^{+} values in the range from 49 to 5.4×10^4.

$$cis^{2+} + trans^{+} \xrightleftharpoons{K^{2+}/K^{+}} cis^{+} + trans^{2+} \qquad (1)$$

$$cis^{3+} + trans^{2+} \xrightleftharpoons{K^{3+}/K^{2+}} cis^{2+} + trans^{3+} \qquad (2)$$

$$cis^{3+} + trans^{+} \xrightleftharpoons{K^{3+}/K^{+}} cis^{+} + trans^{3+} \qquad (3)$$

The organic group of the nitrile ligands influences the thermodynamics of the systems, and $E°$ for the various redox steps increases linearly with the Hammett's σ_p constant of the phenyl substituent (Figure 4c and d) (correlation factor above 0.90):

$$E°(trans^{2+/+}) = 0.340\sigma_p + 0.396 \qquad (4)$$

$$E°(trans^{3+/2+}) = 0.452\sigma_p + 1.433 \qquad (5)$$

$$E°(cis^{2+/+}) = 0.257\sigma_p + 0.503 \qquad (6)$$

$$E°(cis^{3+/2+}) = 0.401\sigma_p + 1.463 \qquad (7)$$

An increase in the electron-withdrawing ability of the substituent results in an increase of the first and second oxidation potentials of both the trans and the cis complexes, in accord with the expected[9,29] stabilization of the HOMO. The energy of this orbital is more sensitive to a change of the nitrile substituent in the area of the trans isomers relative to the corresponding cis ones (larger slopes for the former isomers), and the dependence of the ratios of the isomeric equilibrium constants on the electronic effects of the substituents is given by eqs 8−10.

$$\ln(K^{2+}/K^{+}) = -3.23\sigma_p + 4.17 \qquad (8)$$

$$\ln(K^{3+}/K^{2+}) = -1.99\sigma_p + 1.05 \qquad (9)$$

$$\ln(K^{3+}/K^{+}) = -5.22\sigma_p + 5.22 \qquad (10)$$

The greater sensitivity of the trans isomers to the electronic effects of the nitrile substituents is also apparent through spectroscopic and structural properties of the complexes. In fact, $\nu(N{\equiv}C)$ for the trans isomers is lower than for the analogous cis compounds,[30] whereas the X-ray data[31] for *trans*- and *cis*-$[Re(NCC_6H_4Me\text{-}4)_2(dppe)_2]^+$ indicate a weaker π electron release from the metal to the diphosphine ligands in the trans isomer. Hence, the two trans nitrile ligands are behaving as stronger π electron acceptors than in the cis arrangement, therefore participating, to a greater extent, into a delocalized π electronic system involving also the metal and the aryl substituent whose electronic effect is then more effectively transmitted to the metal.

In contrast with the aromatic nitrile complexes, for the *alkyl* nitrile ones the steric influence of R is determinant. In fact, $E°(cis^{+/2+})$ does not increase with the polar σ^* constant of R, but instead increases with its bulkiness: $E°(Me) < E°(CH_2C_6H_4\text{-}Cl\text{-}4) < E°(Pr^i) < E°(Bu^t)$. For the other waves of the cis and trans isomers this sequence is also roughly observed.

Final Comments

This study has allowed us to investigate the relative thermodynamic and kinetic stabilities of the cis/trans isomeric pairs of series of 18- and 16-electron octahedral-type complexes of rhenium with modest π electron acceptor ligands (organonitriles) and their dependence on the electronic and steric properties of such ligands.

Stepwise oxidation of the starting 18-electron complexes results in thermodynamic and kinetics gains toward the trans isomers. The latter ones are the thermodynamically favored isomers but kinetic constraints impose that cis-to-trans isomerization occurs only at the 16-electron level. This contrasts with other systems, such as the dicarbonyl phosphinic complexes of group 6 transition metals, for which a single-electron oxidation of the 18-electron cis isomers is sufficient to induce such isomerization. Despite their greater stability in comparison with the corresponding cis isomers, the 16-electron trans complexes are prone to decomposition, which is not observed for the 17- or 18-electron complexes, and conceivably involves a nucleo-

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(29) (a) Pombeiro, A. J. L. *New J. Chem.* **1997**, *21*, 549 and references cited therein. (b) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271. (c) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980. (d) Chatt, J.; Kan, C. T.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2030.

(30) Guedes da Silva, M. F. C.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1996**, *526*, 237.

(31) (a) Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1991**, *403*, C1. (b) Guedes da Silva, M. F. C.; Duarte, M. T.; Galvão, A. M.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1992**, *433*, C14.

philic addition. For the aromatic nitrile complexes, the decomposition rate respond to electronic effects of the phenyl substituents of the nitrile ligands, being promoted by an increase of their electron-withdrawing ability.

The thermodynamics of the cis/trans equilibria at the various metal oxidation levels are also dependent on such electronic effects, the 18- and 17-electron trans isomers being more sensitive than the corresponding cis species. Nevertheless, stereochemical effects have to be taken into account in the case of the alkyl nitrile complexes.

The significance of our system toward the development of a "molecular hysteresis" behavior[32] in terms of the overall double square Scheme 2 is accounted for by the fast two-electron induced isomerization and the rather slow isomerization at the single-electron oxidation level (the hysteresis loop would be broken by such a conversion). These geometrical isomerizations present more favorable rates (faster by a factor of ca. 10^2 or slower by a factor of at least ca. $10^{-2}-10^{-3}$, respectively) than the corresponding linkage isomerizations reported by others[32] for some diruthenium complexes. However, the thermodynamically unfavored backward isomerization at the reduced level for our dinitrile complexes prevents an efficient closure of the hysteresis loop. This limitation at the fully reduced level is not found in the above diruthenium systems[32] nor in our mononitrile complexes $[\mathrm{ReCl(NCR)(dppe)_2}]$[17] which thus are particularly promising for the above purpose.

Although at least some of our conclusions appear to present a considerable generality for octahedral-type di- and/or mononitrile complexes of rhenium (in oxidation state I, II, or III) with phosphine coligands, generalizations have to be considered rather cautiously. The electrochemical behavior of coordination compounds which can undergo anodically induced geometrical isomerization is dependent on a delicate balance of kinetic and thermodynamic effects which are determined by a variety of factors, either electronic or steric.

Experimental Section

All the manipulations and reactions were carried out in the absence of air using standard inert-gas flow and vacuum techniques. IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer and ^{1}H, ^{31}P-{^{1}H}, and ^{13}C NMR spectra on a Varian Unity 300 spectrometer. Solvents were purified by standard procedures, and the complexes $[\mathrm{Re(NCR)_2(dppe)_2}][\mathrm{BF_4}]$ [R = $\mathrm{C_6H_4X}$-4 (X = $\mathrm{NEt_2}$, OH, OMe, Me, H, F, Cl), $\mathrm{Bu^t}$, $\mathrm{Pr^i}$, $\mathrm{CH_2C_6H_4Cl}$-4] were prepared by a published method[31] and fully identified by IR spectroscopy, ^{1}H, ^{31}P, ^{13}C, or ^{19}F NMR spectrometry. The previously unreported complex *cis*-$[\mathrm{Re(NCMe)_2(dppe)}]$Cl were obtained as follows.

A suspension of *trans*-$[\mathrm{ReCl(N_2)(dppe)_2}]$ (0.41 g, 0.39 mmol) in NCMe (100 cm^3, 1.9 mol) and $\mathrm{C_6H_6}$ (100 cm^3) was stirred for 72 h under argon and under 150 W tungsten lamp irradiation. Concentration of the solution led to the precipitation of greenish yellow crystals which were filtered off, washed with NCMe and then with NCMe/pentane, and dried *in vacuo*. Further crops could be obtained from the filtered solution but they were frequently contaminated with other unidentified products (ca. 40% yield). IR (Nujol mull in CsI pellet): ν(NC), 2230 (s), 2220 (sh). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 7.30−6.77 (m, 32H, dppe), 6.73 (t, J = 7.8 Hz, 4 H_{ortho}, dppe), 6.45 (t, J = 7.8 Hz, 4H_{ortho}, dppe), 2.62 (m, 8H, $\mathrm{CH_2}$, dppe), 1.87 (s, 6H, NCMe). ^{31}P NMR ($\mathrm{CD_2Cl_2}$): δ [ppm rel. $\mathrm{P(OMe)_3}$] −100.1 (s) and −103.4 (s). Anal. Calcd for $\mathrm{C_{56}H_{54}N_2P_4ClRe}$: C, 61.1; H, 4.9; N, 2.5. Found: C, 61.2; H, 5.5; N, 2.3.

The electrochemical experiments were performed either on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PAR 175 universal programmer connected to a Nicolet-310 Digital Oscilloscope, or on an EG&G PAR 273A potentiostat/galvanostat connected to a 386-SX personal computer through a GPIB interface.

Cyclic voltammograms were obtained in 0.2 mol dm^{-3} solutions of $[\mathrm{Bu_4N}][\mathrm{BF_4}]$ in $\mathrm{CH_2Cl_2}$, at a platinum-disc working electrode (0.5 mm diameter) whose potential was controlled vs a Luggin capillary connected to a silver wire pseudo-reference electrode; a Pt auxiliary electrode was employed.

Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The two compartments were separated by a glass frit and equipped with platinum gauze working and counter electrodes. A Luggin capillary connected to a silver wire pseudo reference electrode was used to control the working electrode potential. All manipulations were carried out under dinitrogen. The redox potentials of the complexes are given in volts vs SCE and determined by using as a postcalibration internal reference the $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})]^{0/+}$ couple (E° = 0.525V vs SCE).

The simulations of the cyclic voltammograms of the cis isomers were carried out by using the specific program and the method reported previously,[17] but, for the determination of the kinetic rate constant for the decomposition of *trans*$^{3+}$, the conventional CVSIM program[24] was employed. They are reported only for the complexes that were isolated in analytically pure form. The ratios of the equilibrium constants K^{n+} (n = 1−3) were estimated by considering that $\Delta G^\circ = 0$ for each thermochemical cycle represented in Scheme 2 and the measured E° values for the corresponding redox steps.

Acknowledgment. This work was partially supported by the JNICT (The National Board for Scientific and Technological Research, Portugal)−CNRS (Centre National de la Recherche Scientific, France) Cooperation Programme, by the FCT (Foundation for Science and Technology, Portugal), and by the PRAXIS XXI Programme (Portugal), CNRS, ENS, and MESR (France).

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(32) (a) Sano, M.; Taube, H. *Inorg. Chem.* **1994**, *33*, 705. (b) Sano, M.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 2327.