Bioinorganic and Organometallic Compounds", A.J.L. Pombeiro and J. McCleverty (eds.), NATO ASI Series, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1993, 411.

[3] - J. Vasilevskis and D.C. Olson, Inorg. Chem., 1971, 10, 1228.

Acnowledgements

This work has been partially supported by the PEDIP programme (Y.Y.T.), INIC and JNICT (Portugal).

---

# ANODICALLY INDUCED *cis* to *trans* ISOMERIZATION of the NITRILE COMPLEXES [ReCl(NCR)(dppe)$_2$]

**M.FÁTIMA C. GUEDES da SILVA, JOÃO J.R. FRAÚSTO da SILVA and ARMANDO J.L. POMBEIRO**

*Centro de Química Estrutural, Complexo I, I.S.T.*
*Av. Rovisco Pais, 1096 Lisboa codex, Portugal*

## ABSTRACT

Reaction of *trans*-[ReCl($N_2$)(dppe)$_2$] (dppe=$Ph_2PCH_2CH_2PPh_2$) with NCR (R=aryl) in toluene and under sunlight gives the corresponding *cis*-[ReCl(NCR)(dppe)$_2$] compounds. The electrochemistry of these complexes in 0.2M [$Bu_4N$][$BF_4$]/THF is studied by cyclic voltammetry and controlled potential electrolysis, at Pt electrodes, which indicate the occurrence of an electroinduced *cis*-to-*trans* isomerization.

In pursuit of our studies on the coordination chemistry of small molecules, particularly C-N and C-C unsaturated species, at dinitrogen-binding metal sites [1], we have succeeded in preparing a series of *cis* and *trans* rhenium(I)-nitrile complexes involving the {Re(dppe)$_2$}$^+$ metal centre.

Extended Hückel MO calculations [2] indicate that for octahedral type phosphine complexes, namely of group 6 transition metals with CO and $N_2$ ligands, the relative stability of the *cis* and *trans* isomer depends on the oxidation state of the metal, with preference of the *cis* geometry for the 18-electron compounds,and the *trans* geometry for the 17-electron species. However, for related 18-electron Re(I) and Tc(I) complexes, such as [MLL'(dppe)$_2$]$^+$ or [MXL(dppe)$_2$] (M=Re [3] or Tc [4]; X=Cl or H; L,L'=CO, $N_2$, CNR, etc.), the *trans* geometry of the phosphine appears to be favoured, though some exceptions have already been reported by us [5].

We have now succeeded in the synthesis of *cis*-[ReCl(NCR)(dppe)$_2$] by reacting the parent *trans*-[ReCl($N_2$)(dppe)$_2$] with the apropriate nitrile in toluene and under sunlight (eq.1). The *trans* isomers can be prepared in the oxidized form by chemical or electrochemical oxidation of the *cis* or derived hydride species, whereas the neutral *trans* form is obtained by deprotonation or cathodic reduction of methyleneamido or hydride complexes, respectively.

$$trans\text{-}[ReCl(N_2)(dppe)_2] + NCR \rightarrow cis\text{-}[ReCl(NCR)(dppe)_2] + N_2 \qquad (1)$$

By cyclic voltammetry at a Pt disc electrode, the neutral *cis* and *trans* rhenium-nitrile compounds $[ReCl(NCR)(dppe)_2]$, in 0.2M $[Bu_4N][BF_4]$/THF, exhibit two successive one-electron anodic processes (Fig., waves I and II in each case). Although the second anodic wave (II) occurs at analogous potentials for both isomers, the first one (I) exhibits an oxidation potential which is clearly dependent on the isomer (Table). Indeed, the *trans* isomers are oxidised at a considerably lower potential than the corresponding *cis* compounds, thus indicating that the HOMO of the latter is lower in energy than the HOMO of the former, in agreement with the above mentioned [2] MO theoretical studies.

Table: Half-wave oxidation potentials (V *vs.* s.c.e.) for *cis*- and *trans*-$[ReCl(NCR)(dppe)_2]$ ($R=C_6H_4OMe$-4, $C_6H_4Me$-4, $C_6H_4F$-4 or $C_6H_4Cl$-4)

| | *cis* isomer | | *trans* isomer | |
|---|---|---|---|---|
| Wave | I | II | I | II |
| $E_{1/2}^{ox}$ | -0.13<br>\|<br>-0.08 | 0.70<br>\|<br>0.72 | -0.34<br>\|<br>-0.25 | 0.66<br>\|<br>0.71 |

Moreover, for the *cis* complex, and on the reverse scan, after the second oxidation wave, a new electrode process is observed at a considerably lower potential than that for the $cis^{+/0}$ redox couple, being due to the correspondent $trans^{+/0}$ process.

This redox wave of the *trans* isomer is not observed by reversing the scan after the first anodic wave of the *cis* compound, thus indicating that the *trans* species is formed only upon the double oxidation of the *cis*, *i.e.*, according to the overall conversion $cis^{2+} \rightarrow trans^{2+}$ ; the wave corresponding to the $trans^{2+/+}$ process overlaps with that for the $cis^{2+/+}$ reduction (see the cyclic voltammogram depicted in the Fig., run at a scan rate of 200 mV.s$^{-1}$). The reverse electroinduced *trans*-to-*cis* isomerization is not observed in the study of the *trans* complex alone.

Moreover, the intensity of the electrogenerated $trans^{+/0}$ reduction wave decreases with a concomitant increase of the reversibility of the $cis^{0/+}$ wave, for sufficiently faster and lower scan rates; in the former case, a decrease of the extent of isomerization naturally occurs, whereas in the second situation (lower scan rates) a $trans^{+}$ (or $trans^{2+}$) conversion into $cis^{+}$ (or $cis^{2+}$) appears to happen *via* bimolecular processes involving reactions of oxidized *trans* with oxidized *cis* isomers, as exemplified in the simplified Scheme.

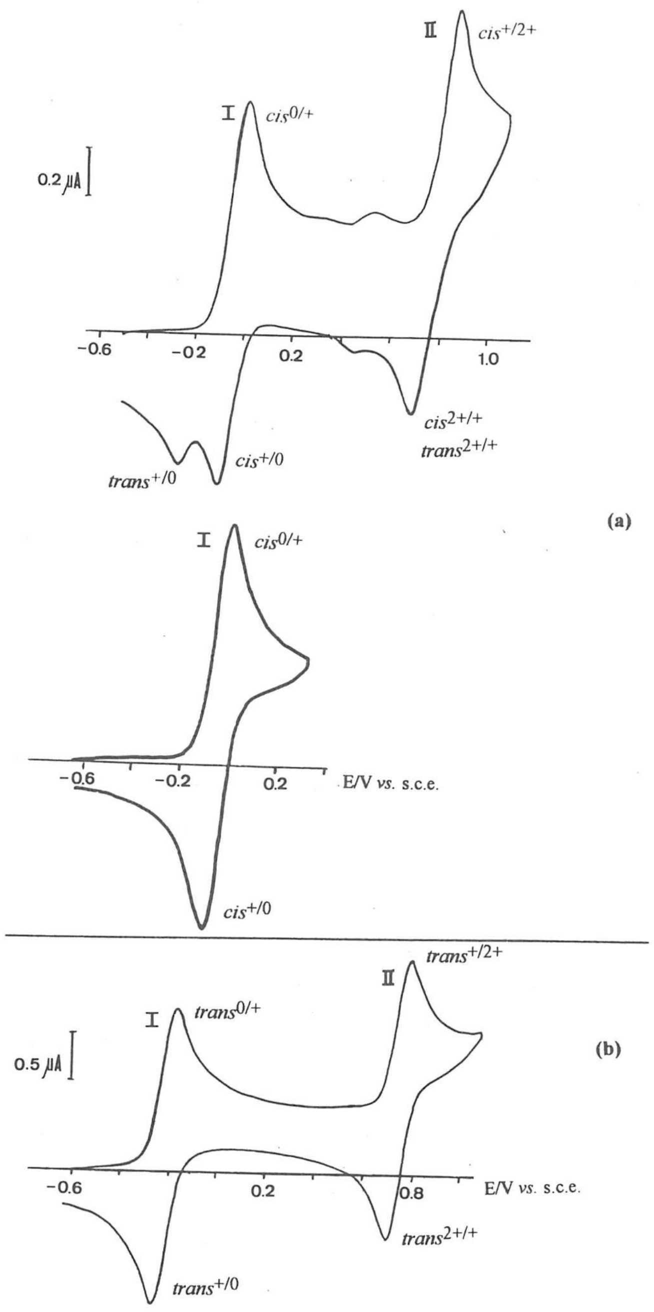
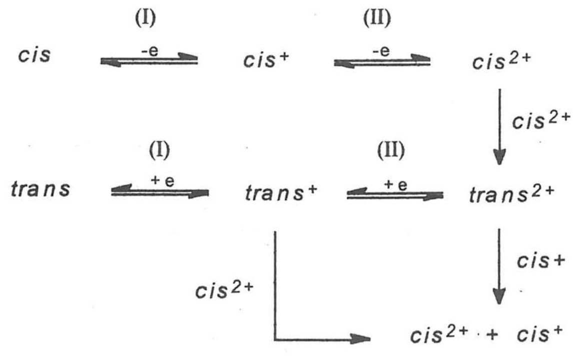
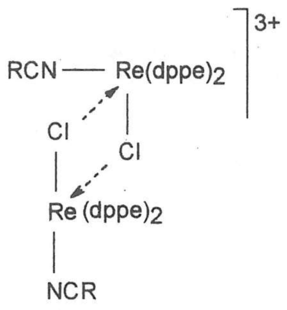


Fig. Cyclic voltammogram for complexes (a) *cis*- and (b) *trans*-$[ReCl(NCR)(dppe)_2]$ ($R=C_6H_4Me$-4) in 0.2M $[Bu_4N][BF_4]$/THF at a Pt disc electrode. Scan rate of 200 mV.s$^{-1}$, T=25°C.



**Scheme**

The bimolecular nature of these isomerization reactions can be interpreted by *postulating* a nucleophilic attack of a chloride ligand of one molecule to the cationic metal centre of another one, thus generating dinuclear intermediates such as the following one, conceivably involved in the $(trans^{+} + cis^{2+})$ or $(trans^{2+} + cis^{+})$ conversion to $(cis^{2+} + cis^{+})$:



By using computer simulation methods, we are currently testing the above mentioned proposed scheme, and investigating other associated reactions and their kinetics.

ACKOWLEDGEMENTS

This work has been partially suported by JNICT and INIC.

REFERENCES

[1] A.J.L.Pombeiro and R.L. Richards, *Coord.Chem.Rev.*, 104 (1990) 13; A.J.L.Pombeiro, *Inorg.Chim.Acta*, 198-200 (1992) 179 ; A.J.L.Pombeiro *J. Organomet.Chem.*, 358 (1988) 273.

[2] D.M.P.Mingos, *J.Organomet.Chem.*, 179 (1979) C29; D.L Dubois and R.Hoffman, *Nouv.J.Chim.*, 1 (1977) 479; J.N.Murrel, A.Al-Derzi, G.J.Leigh and M.F.Guest, *J.Chem.Soc.Dalton Trans.*, (1980) 1425.

[3] A.J.L. Pombeiro, *Inorg. Chim. Acta*,103 (1985) 95; M.F.C.G. Silva, A.J.L.Pombeiro, A.Hills, D.L.Hughes and R.L.Richards, *J.Organomet.Chem.*, 403 (1991) C1; M.F.N.N.Carvalho and A.J.L.Pombeiro, *J.Chem.Soc.Dalton Trans.*, (1989) 1209; A.J.L.Pombeiro, C.J.Pickett and R.L.Richards, *J.Organomet.Chem.*, 224 (1982) 285; A.J.L.Pombeiro, D.L.Hughes and R.L.Richards, *J.Chem.Soc., Chem.Commun.*, (1988) 1052; D.L.Hughes, A.J.L.Pombeiro, C.J.Pickett and R.L.Richards, *J.Chem.Soc., Chem.Commun.*, (1984) 992; A.J.L.Pombeiro, S.S.P.R.Almeida, M.F.C.G.Silva, J.C.Jeffery and R.L.Richards, *J.Chem.Soc.Dalton Trans.*, (1989) 2381.

[4] U.Abram, S.Abram, R.Beyer, R.Muenze, L.Kaden, B.Lorenz and M.Findeisen, *Inorg. Chim. Acta*, 148 (1988) 141; V.Y.T.Struchkov, A.S.Bazanov, L.Kaden, B.Lorenz, M.Wahren, and H.Meyer, *Z.Anor.Allg.Chem.*, 494 (1982) 91.

[5] M.F.C.Guedes da Silva, M.T.Duarte, A.M.Galvão, J.J.R.Fraústo da Silva and A.J.L.Pombeiro, *J. Organomet. Chem.*, 433 (1992) C14.