

STUDY OF THE REDOX BEHAVIOUR OF  $[\text{Bu}_4\text{N}][\text{ReCl}(\text{CN})(\text{dppe})_2]$   
AND OF SOME ALKYLATION PRODUCTS

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**Summary**

The cyclic voltammetric behaviour of *trans*- $[\text{ReX}(\text{CN})(\text{dppe})_2][\text{NBu}_4]$  (X=Cl or H) and of products derived from alkylation, such as *trans*- $[\text{ReH}(\text{CNMe})(\text{dppe})_2]$ , in aprotic medium and at a Pt electrode, is reported.

**Introduction**

Within our interest on the study of the activation through coordination of molecules with synthetic interest, we engaged on the preparation of some rhenium-cyanide complexes [1]. The  $\{\text{ReCl}(\text{dppe})_2\}$  metal centre was chosen since it is known to be able to coordinate a full range of small molecules such as isocyanides [2,5,6], alkynes [3], nitriles [4], etc..

Of particular interest would be the comparison of the redox properties of the cyanide with the isocyanide complexes, and the study of the possible conversion of the former into the latter by alkylation. The redox potentials of *trans*- $[\text{ReCl}(\text{CNR})(\text{dppe})_2]$  are dependent on the electronic properties of R and the omission of this group (compare the cyanide with the isocyanide ligand) should have a pronounced effect on the redox potential, in particular if isoelectronic anionic species could be obtained, such as *trans*- $[\text{ReX}(\text{CN})(\text{dppe})_2]^-$  (X=Cl or H).

**Results and discussion**

The cyanide complex *trans*-[ReCl(CN)(dppe)<sub>2</sub>][Bu<sub>4</sub>N] was obtained via dinitrogen replacement at the precursor *trans*-[ReCl(N<sub>2</sub>)(dppe)<sub>2</sub>]. *trans*-[ReH(CN)(dppe)<sub>2</sub>][Bu<sub>4</sub>N] is formed as a side product in the same reaction probably as a result of the presence of some moisture in the cyanide salt. These compounds present unusual rhenium (I) complex anions and display, by cyclic voltammetry, several redox processes, as indicated in figure 1 for *trans*-[ReCl(CN)(dppe)<sub>2</sub>][Bu<sub>4</sub>N].

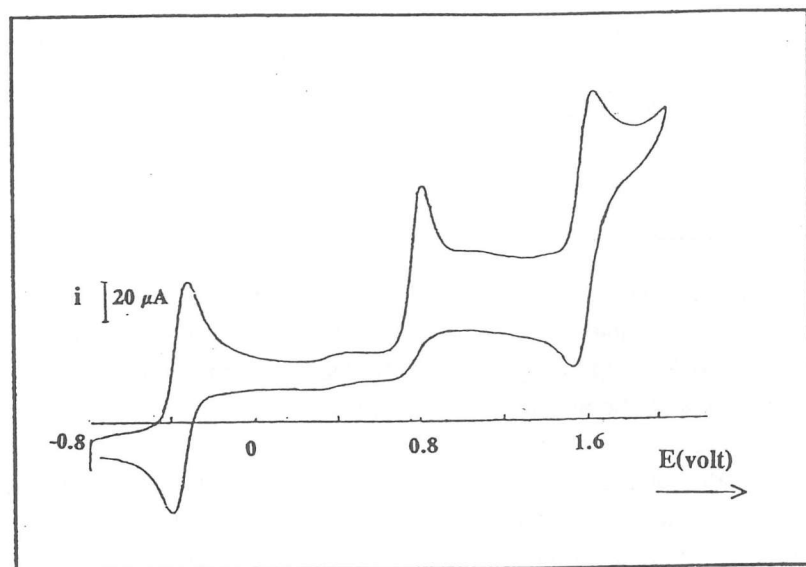


Figure 1- Cyclic voltammogram of *trans*-[ReCl(CN)(dppe)<sub>2</sub>][Bu<sub>4</sub>N], in 0.2M CH<sub>2</sub>Cl<sub>2</sub>/ [Bu<sub>4</sub>N][BF<sub>4</sub>], at a Pt electrode.

The values of the oxidation potential corresponding to the Re(I)->Re(II) and Re(II)->Re(III) processes for the rhenium-cyanide compounds are shown in Table 1. The first anodic process occurs at a considerably lower potential than those recorded for the Re(I)->Re(II) oxidation processes in the neutral compounds (see Table 2), in agreement with the anionic character of the cyanide ligand and its complexes.

Table 1 Redox potentials<sup>(a)</sup> for Re(I)/Re(II) and Re(II)/Re(III) processes measured by cyclic voltammetry.

Complex	E <sub>1/2</sub>	
	Re(I/II)	Re(II/III)
<i>trans</i> -[ReCl(CN)(dppe) <sub>2</sub> ][Bu <sub>4</sub> N] <sup>(b)</sup>	-0.44	0.80 (c)
<i>trans</i> -[ReH(CN)(dppe) <sub>2</sub> ][Bu <sub>4</sub> N]	-0.52	0.80(d)
<i>trans</i> -[ReH(CNMe)(dppe) <sub>2</sub> ] <sup>(e)</sup>	-0.10	0.70 (f)
<i>trans</i> -[ReCl(CN)(dppe) <sub>2</sub> ]	-0.48(g)	0.75

(a) Values in volt vs. sce; ferrocene (E<sub>1/2</sub><sup>ox</sup>=0.545V) used as internal standard and values measured in 0.2M [Bu<sub>4</sub>N][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> unless stated otherwise. (b) *trans*-[ReCl(N<sub>2</sub>)(dppe)<sub>2</sub>] (E<sub>1/2</sub><sup>ox</sup> = 0.28V) used as reference. (c) This process has a considerable degree of irreversibility, ip<sup>ox</sup>/ip<sup>red</sup> = 1.8. (d) Irreversible wave (E<sub>p</sub><sup>ox</sup>). (e) In MeCN. (f) Irreversible wave (E<sub>p</sub><sup>ox</sup>); another oxidation wave at E<sub>p</sub><sup>ox</sup> = 0.96 V is also observed. (g) Cathodic wave.

Cyanide behaves as a considerably stronger net electron donor than isocyanide, carbonyl or dinitrogen and, from the value of |E<sub>1/2</sub><sup>ox</sup> for *trans*-[ReCl(CN)(dppe)<sub>2</sub>]<sup>-</sup> and the knowledge [5] of E<sub>s</sub> and β for the {ReCl(dppe)<sub>2</sub>} site one can estimate, for CN<sup>-</sup>, a P<sub>L</sub> value of -0.33V.

Table 2 Redox potentials (V vs. s.c.e.) for the Re(I)->Re(II) oxidation in diphos systems

Complex	E <sub>1/2</sub>	Reference
[ReCl(CN)] <sup>-</sup>	-0.44	This work
[ReCl(NCBut <sup>t</sup> )]	-0.14	[7]
[ReCl(CNMe)]	0.08	[8]
[ReCl(N <sub>2</sub> )]	0.28	[9]
[ReCl(CNC <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> -2,6)]	0.43	[5]
[ReCl(CO)]	0.63	[8]

[Re] = {Re(dppe)<sub>2</sub>}; dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>

The effect of the substitution of chloride (E<sub>1/2</sub><sup>ox</sup>=-0.44V) by hydride (E<sub>1/2</sub><sup>ox</sup>=-0.52V) in *trans* position to the cyanide ligand corresponds to a small

decrease of the oxidation potential for the complex in agreement with the slightly higher net electron donor ability of the hydride ligand  $\{P_L(H^-) = -1.22 \leq P_L(Cl^-) = -1.19V$  [10].

As a consequence of the low oxidation potentials observed for the rhenium-cyanide complexes, they are easily oxidized either by air or other oxidants. Oxidation is the main process detected upon reaction of *trans*-[ReCl(CN)(dppe)<sub>2</sub>][Bu<sub>4</sub>N] with *sec*-butyl iodide to give *trans*-[ReCl(CN)(dppe)<sub>2</sub>]. The study of the electrochemical behaviour of this compound confirms the oxidation state +2 of the metal, since a cathodic wave is observed at the expected redox potential.

Complexes *trans*-[ReX(CN)(dppe)<sub>2</sub>][Bu<sub>4</sub>N] are difficult to study in coordinating solvents, such as tetrahydrofuran or acetonitrile, since coordination of the solvent can apparently occur and new species are formed as can be observed by i.r. spectroscopy.

However, alkylation of the cyanide ligand by Me<sub>3</sub>SiCF<sub>3</sub>SO<sub>3</sub> gives *trans*-[ReH(CNMe)(dppe)<sub>2</sub>], authenticated by an X-ray analysis [1]. The mechanism for the reaction is not completely understood, but moisture in the highly hygroscopic trimethylsilyl triflate could account for the presence of the hydride.

As expected from the P<sub>L</sub> values for the hydride and the chloride co-ligands (see above), *trans*-[ReH(CNMe)(dppe)<sub>2</sub>] presents a slightly lower oxidation potential ( $E_{1/2}^{ox} = -0.10V$ ) than *trans*-[ReCl(CNMe)(dppe)<sub>2</sub>] ( $E_{1/2}^{ox} = 0.08V$ ).

Other reactions of the rhenium-cyanide species with electrophiles are under study. Of particular interest is the reaction with acid; however, a mixture of products resulting from attack at the cyanide and/or the metal is obtained.

#### Final comments

Coordinated cyanide at *trans*-[ReCl(CN)(dppe)<sub>2</sub>][NBu<sub>4</sub>] can be alkylated to afford the corresponding isocyanide complex. However the high electron density of the metal centre seems to be able to direct the electrophilic attack towards both the cyanide ligand and the rhenium metal. The dominant route depending on the electrophile. Bulky alkylating agents, such as *sec*-butyl iodide, are not able to alkylate and oxidation of the cyanide complex occurs. However, reaction with Me<sub>3</sub>Si<sup>+</sup> affords the methyl isocyanide species, but a formal replacement by hydride also occurs, and

*trans*-[ReH(CNMe)(dppe)<sub>2</sub>] is obtained. A small electrophile, such as the proton, reacts in a number of ways, as observed by cyclic voltammetry, and a mixture of the isocyanide (CNH), carbyne (CNH<sub>2</sub>) and probably of the hydride-isocyanide species appears to be obtained.

The slightly higher electron releasing ability of hydride compared to chloride accounts for the relative oxidation potentials of the corresponding complexes *trans*-[ReX(CN)(dppe)<sub>2</sub>][NBu<sub>4</sub>] (X=H or Cl) and *trans*-[ReX(CNMe)(dppe)<sub>2</sub>].

#### Acknowledgements

This work was partially supported by the Instituto Nacional de Investigaç o Cient fica and the Junta Nacional de Investigaç o Cient fica e Tecnol gica.

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