

## Redox Properties of Some Cyanamide - Derived Complexes of Palladium (II) or Platinum (II)

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### Introduction

The coordination chemistry of cyanamide ( $\text{N}\equiv\text{CNH}_2$ ) or derived compounds remains virtually unexplored and, within our interest on the activation of such species by transition metal centres [1], we have prepared some complexes of Pd(II) or Pt(II) of the following types: *trans*- $[\text{MCl}_2\text{L}_2]$  ( 1, M = Pd or Pt; L =  $\text{NCNMe}_2$  or  $\text{NCNEt}_2$  ), *trans*- $[\text{Pt}(\text{CF}_3)\text{L}(\text{PPh}_3)_2][\text{BF}_4]$  [2, L =  $\text{NCNMe}_2$ ,  $\text{NCNEt}_2$  or  $\text{NCNC}(\text{NH}_2)_2$  (cyanoguanidine)], *trans*- or *cis*- $[\text{PtClL}(\text{PPh}_3)_2][\text{BPh}_4]$  [ 3, L =  $\text{NCNH}_2$ ,  $\text{NCNMe}_2$ ,  $\text{NCNEt}_2$  or  $\text{NCNC}(\text{NH}_2)_2$ ].

Although their syntheses and spectroscopic properties are reported separately, we now present their electrochemical behaviour, as well as that of the free cyanamides, as investigated by cyclic voltammetry ( CV ) and controlled potential electrolysis ( CPE ) in 0.2 M  $[\text{NBu}_4][\text{BF}_4]$  /  $\text{NCMe}$  at a Pt-disc or -gauze electrode, respectively.

## Results and discussion

### A - Cyanamides

All the free cyanamides present, by CV, an irreversible anodic wave at  $E_p^{ox}$  in the range 2.0 - 2.5 V vs. SCE, involving, by CPE, a single-electron (NCNH<sub>2</sub>), a two-electron [NCNC(NH<sub>2</sub>)<sub>2</sub>] or a three-electron (NCNMe<sub>2</sub> or NCNEt<sub>2</sub>) process. The oxidation is conceivably centred at the amine group and possibly leads to H<sup>+</sup> liberation followed by further reaction (such as dimerization) of the radical product. The evolution of H<sup>+</sup> can result from the cleavage of an anodically activated N - H bond (in an  $\overset{+}{N}H_2$  group of oxidized cyanamide or cyanoguanidine) or NC - H bond (in the  $\overset{+}{N}Me_2$  or  $\overset{+}{N}Et_2$  groups of the oxidized organocyanamides).

An irreversible cathodic process is detected by CV only for cyanamide and cyanoguanidine at  $E_p^{red}$  ca. - 1.6 V. It appears to correspond to a single electron transfer as measured by CPE and conceivably involves the reduction of the imino  $-N=C<$  group (followed by protonation of the radical anion and further reactivity), as known [2] to occur, at similar potentials, for Schiff bases.

### B - Cyanamide complexes

#### B.1 - Anodic behaviour

The neutral dicyanamide complexes *trans*-[MCl<sub>2</sub>(NCNR<sub>2</sub>)<sub>2</sub>] (1, M = Pd or Pt, R = Me or Et) present, by CV, an irreversible anodic wave at  $E_p^{ox}$  ca. 2.5 V (a potential similar to those exhibited by the free organocyanamides) which, by CPE, involves ca. 6 electrons, being ascribed to an overall anodic process centred at both the cyanamide ligands. Another irreversible anodic wave can also be observed by CV at

ca. 1.7 ~ 1.8 V; however, it displays a much lower current intensity (involving, e.g., by CPE, only 0.1 electron / molecule for 1, M = Pt, R = Et) and is absent in the case of (1, M = Pd, R = Et), thus possibly being due to a decomposition product or to a contamination of the samples.

The cationic mono-cyanamide complexes *trans*-[Pt(CF<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] (2) exhibit, by CV, an irreversible anodic wave at  $E_p^{ox}$  ca. 2.3 - 2.4 V, involving, by CPE, ca. 2 electrons [for L = NCNC(NH<sub>2</sub>)<sub>2</sub>] or ca. 3 electrons (for L = NCNMe<sub>2</sub>), as observed in the free cyanamide ligand. Hence, it should correspond to an anodic process centred at the single cyanamide ligand.

Such a process, however, is not observed at complexes (3), i.e., *cis*-[PtCl(L)(PPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>] [L = NCNH<sub>2</sub> or NCNC(NH<sub>2</sub>)<sub>2</sub>] and *trans*-[PtCl(L)(PPh<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>] (L = NCNMe<sub>2</sub> or NCNEt<sub>2</sub>), whose cyclic voltammograms only exhibit the two anodic waves typical of the BPh<sub>4</sub><sup>-</sup> counter-ion (at  $E_p^{ox}$  = 0.99 and 1.96 V, the latter wave with a higher intensity than the former one). This behaviour suggests that, for the cationic mono-cyanamide complexes, the chloride ligand (in 3) has a significant stabilizing effect on the HOMO (relative to the CF<sub>3</sub> ligand in 2).

#### B.2 - Cathodic behaviour

An irreversible cathodic wave has been observed by CV only for the neutral Pt complexes *trans*-[PtCl<sub>2</sub>(NCNR<sub>2</sub>)<sub>2</sub>] (1, R = Me or Et) and for the cationic compounds *trans*-[Pt(CF<sub>3</sub>)L(PPh<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>] [2, L = NCNR<sub>2</sub> or NCNC(NH<sub>2</sub>)<sub>2</sub>]. In the latter it occurs at a less cathodic potential ( $E_p^{red}$  ca. - 1.5 V) than in the former complexes ( $E_p^{red}$  ca. - 1.8 ~ - 2.0 V), in agreement with the expected charge effect, and in both cases it involves, by CPE, ca. 1 ~ 1.5 electrons / molecule. The cathodic wave was never detected in any of the Pd complexes and such a metal dependence, as well as the weak sensitivity of the cathodic behaviour to the cyanamide ligand (in particular the analogy observed for complexes 2 with either cyanoguanidine or

organocyanamide ligands, and the occurrence of the cathodic process in complexes with organocyanamide ligands which, when uncoordinated, do not display any cathodic wave) suggest that the cathodic process involves the metal reduction. In agreement, complexes ( 1 ) display  $E_{p}^{red}$  at values ( - 1.8 to - 2.0 V ) which are very similar to that observed ( - 1.97 V ) [ 3 ] for the reduction of the related *trans*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] complex which is believed to be centred at the metal [Pt(II) → Pt(0)].

The non detection of any cathodic wave in complexes ( 3 ), whereas it is observed in ( 2 ), suggests that, in these cationic species, the chloride ligand presents, relative to CF<sub>3</sub>, a destabilizing effect on the LUMO.

#### References

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## STRUCTURE-POTENTIAL RELATIONSHIPS FOR THE NITRILE COMPLEXES *trans*-[FeBr(NCR)(Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>)<sub>2</sub>][BF<sub>4</sub>]

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#### SUMMARY

The electrochemical behaviour, in aprotic medium, of the 18-electron octahedral-type nitrile complexes *trans*-[FeBr(NCR)(depe)<sub>2</sub>][BF<sub>4</sub>] (R = alkyl or aryl, depe = Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>) was studied by cyclic voltammetry and controlled potential electrolysis. They undergo two successive single-electron reversible oxidations and electrochemical ligand and metal site parameters [which measure the electronic properties of the nitrile ligands and their binding iron(II) or iron(III) centre] were estimated from the measured half-wave oxidation potential values.

#### RESULTS AND DISCUSSION

The electrochemical behaviour of the complexes *trans*-[FeBr(NCR)(depe)<sub>2</sub>][BF<sub>4</sub>] (R = alkyl or aryl, depe = Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>) was studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), in 0.2 M [NBu<sub>4</sub>][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub>, at a Pt-wire or -gauze electrode, respectively, at low temperature (-10 to -65 °C) in view of their rapid decomposition in solution at higher temperatures.

These complexes exhibit, by CV, two successive single-electron reversible oxidations at  $E_{1/2}^{ox}$  ca. 0.63 to 0.91 V and  $E_{1/2}^{ox}$  ca. 1.35 V vs. S.C.E., respectively (Fig. 1). The first anodic wave is assigned to the Fe(II) to Fe(III) oxidation and the second one to the Fe(III/IV) redox couple. A single-electron irreversible cathodic wave