A considerably different redox behaviour is detected for the first raw (Fe and Cu) compared to second (Pd) and third raw (Pt) complexes, since on iron and copper complexes the reduction processes have a metal centred character. However, the two types of ligands seem to have different behaviours when they bind metals such as palladium or platinum. In fact, the redox processes observed at complexes derived from type (B) ligands seem to display considerable ligand character, in contrast with complexes derived from type (A) ligands for which the cathodic processes appear to have usually a considerable metal character, possibly as a consequence of different participation of these ligands on the LUMO and on the HOMO of the complexes.

Camphor imine species are versatile ligands under the coordenative point of view, which bind the different metal sites through one of the available imine nitrogen atoms, adapting themselves to the characteristics of the transition metal. Moreover, at the iron and copper centres they possibly act as chelating ligands such as observed before[4] on copper complexes, in contrast with the monodentate coordination observed on metal sites of the second and third raws.

They also display high electronic versatility, stabilizing metal centres with considerably different redox properties.

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Electrochemical behaviour of adducts of *trans*-[Mo(NCN)₂(dppe)₂] with some transition metal Lewis acids

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Abstract

The electrochemical behaviours of the bis(cyanoimide) complex *trans*-[Mo(NCN)₂(dppe)₂] (dppe=Ph₂PCH₂CH₂PPh₂) and of the derived adducts with some transition metal [Pt(II), Re(I) or V(III)] Lewis acids have been investigated by cyclic voltammetry (CV) and, in some cases, by controlled-potential electrolysis (CPE), in aprotic media, at a Pt electrode. In general, anodic and cathodic processes are detected, by CV, being centred either at the Mo or at the other transition metal site, and the effect of the formation of the adduct on the redox potential is discussed, as well as the dependence of its stability on the electron-transfer process.

Introduction

The synthesis and study of the reactivity of compounds exhibiting enzyme-like activity is a major challenge in Chemistry. In pursuit of our interest in the activation by transition metal centres of alternative substrates of nitrogenase, we have been investigating the activation of cyanamide, a recently discovered substrate of this enzyme, by dinitrogen binding sites, and, *e.g.*, we obtained the bis(cyanoimide) complex *trans*-[Mo(NCN)₂(dppe)₂] (dppe=Ph₂PCH₂CH₂PPh₂) from the reaction of cyanamide with the parent dinitrogen complex, *trans*-[Mo(N₂)₂(dppe)₂].

In the cyanoimido-complex, one of the NCN ligands (or, in one of the cases, both of them - see below) undergoes electrophilic attack by a transition metal Lewis acid (MLₙ), *e.g.*, derived from [Pt₂Cl₄(PEt₃)₂], [ReCl(N₂)(PMePh₂)₄] or [VCl₃(THF)₃], to form the corresponding dinuclear adduct of the type *trans*-[Mo(NCN→MLₙ₋₁)(NCN)(dppe)₂] (or the trinuclear product if both the NCN ligands bind to MLₙ₋₁ centres).

We now report the results of an electrochemical study of both the bis(cyanoimide) complex and the corresponding adducts, by CV and, in some cases, by CPE.

The complex *trans*-[Mo(NCN)$_2$(dppe)$_2$] was prepared according to a published procedure [1] and the solvents were dried and degassed by using standard techniques. The electrochemical experiments were carried out on an EG&G PAR 273A potenciostat/galvanostat connected to a 386-SX personal computer through a GPIB interface. CV and CPE were undertaken in a two-compartment three-electrode cell, at a platinum disc working electrode ($\phi = 0.5$ mm or 1.5 mm) for CV or at a platinum-gauze working electrode for CPE, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode, in 0.2M [NBu$_4$][BF$_4$] / CH$_2$Cl$_2$ or THF. The redox potentials are quoted relative to the SCE by using as internal reference the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ couple ($E_{1/2}^{ox} = 0.525$ V *vs*. SCE in 0.2M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ or $E_{1/2}^{ox} = 0.545$ V *vs*. SCE in 0.2M [NBu$_4$][BF$_4$]/THF).

Results and discussion

Starting bis(cyanoimide) complex *trans*- [Mo(NCN)$_2$(dppe)$_2$]

This complex shows, by CV, an irreversible cathodic wave ($E_p^{red} = -1.82$ V), involving (CPE) a two-electron process, assigned to the Mo(IV/II) reduction. It also undergoes a single-electron reversible oxidation ($E_{1/2}^{ox} = 0.71$ V), assigned to the Mo(IV/V) oxidation, followed, at higher potentials, by a second irreversible wave ($E_p^{ox} = 1.34$ V).

[Pt$_2$Cl$_4$(PEt$_3$)$_2$] and the derived diadduct [Mo{NCN→PtCl$_2$(PEt$_3$)}$_2$(dppe)$_2$]

The dinuclear [Pt$_2$Cl$_4$(PEt$_3$)$_2$] complex, in solution, undergoes Cl-bridge cleavage, giving [PtCl$_2$(PEt$_3$)S] (S is a solvent molecule). Hence, the observed electrochemical behaviour concerns the product of the cleavage, which exhibits two irreversible cathodic waves, at $^IE_p^{red} = -1.44$ V and $^{II}E_p^{red} = -1.68$ V (CH$_2$Cl$_2$). They involve reduction of Pt(II) with possible cleavage of a Pt-Cl bond (liberation of chloride). An anodic wave is detected at 1.30 V, but only upon scan reversal following the cathodic reduction.

The CV of the trinuclear adduct [Mo{NCN→PtCl$_2$(PEt$_3$)}$_2$(dppe)$_2$] (Fig. 1) displays two successive single electron oxidations, the first one (I) being reversible ($^IE_{1/2}^{ox} = 0.94$ V) and the second one (II) irreversible ($^{II}E_p^{ox} = 1.51$ V). It also shows a reversible cathodic process (III) ($E_{1/2}^{red} = -1.17$ V).
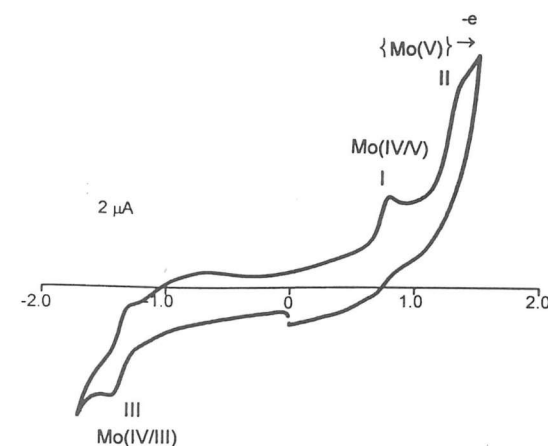
Fig.1. Cyclic voltammogram for a solution of [Mo{NCN→PtCl$_2$(PEt$_3$)}$_2$(dppe)$_2$] (0.976 mM) in 0.2 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$, at a Pt disc working electrode (ϕ=1.5 mm) (scan rate=20 mVs^{-1}; potential in V *vs*. SCE).

The two anodic processes should be centred at the Mo site which, in the adduct, is harder to oxidize (more stabilized HOMO with a dominant metal contribution) than in the parent cyanoimido-complex, in accord with the expected increase of the π-electron release from Mo to the cyanoimido-ligand as a result of its ligation to the Pt centre. A related effect occurs in the reduction, that is, the cathodic wave of the adduct has a shift to higher potentials (stabilization of the LUMO) relative to the cyanoimido-complex, in agreement with the stronger release, in the adduct, of the metal electronic charge to the ligand. Moreover, the absence of the above "non-genuine" anodic wave at 1.30 V, which appears in the case of the Pt Lewis acid alone, also suggests that the cathodic wave of the adduct is centred at the Mo site.

The shifts in redox potentials upon adduct formation are quite significant because it involves the addition of the Lewis acid to both the NCN ligands.

[ReCl(N$_2$)(PMePh$_2$)$_4$] and the derived adduct [Mo{NCN→ReCl(N$_2$)(PMePh$_2$)$_3$}(NCN)(dppe)$_2$]

The CV of the starting dinitrogen complex has two reversible single-electron anodic waves ($^IE_{1/2}^{ox} = 0.24$ V and $^{II}E_{1/2}^{ox} = 1.26$ V). They correspond to the Re(I/II) and Re(II/III) oxidations, respectively.

The adduct has four anodic waves. The first one is reversible ($^IE_{1/2}^{ox} = 0.13$ V), whereas the other three are irreversible ($^{II}E_p^{ox} = 0.63$ V, $^{III}E_p^{ox} = 1.07$ V and $^{IV}E_p^{ox} = 1.35$ V). An irreversible cathodic wave is observed at $E_p^{red} = -1.66$ V.

We consider that the first and the third oxidation waves, which occur at potentials *ca*. 0.1 V less anodic than those of the parent rhenium complex, are centred at the Re site since, in

the adduct, this centre is receiving strong σ-electron charge from the cyanoimido-ligand, thus becoming easier to oxidize.

The other two oxidation waves and the cathodic wave are probably centred at the Mo site, and the values of their redox potentials, in comparison with those of the Pt adduct, differ much less from the corresponding ones for the bis(cyanoimide) complex because the Re(I) centre is a strong π-electron back releaser, possibly also to the new cyanoimido-derived ligand, thus compensating partially for the σ-electron donation of the latter group, and therefore hampering a high variation of electronic density at the Mo centre.

[VCl$_3$(THF)$_3$] and the derived adduct [Mo{NCN→VCl$_3$(THF)$_2$}(NCN)(dppe)$_2$]

The V complex shows, by CV, two irreversible anodic waves ($^{I}E_p^{ox} = 0.94$ V and $^{II}E_p^{ox} \approx$ 1.47 V) assigned to the V(III/IV) and V(IV/V) oxidations, respectively. It also displays two irreversible cathodic processes ($^{I}E_p^{red} = -0.84$ V and $^{II}E_p^{red} = -1.07$ V), conceivably corresponding to the V(III/II) and (VII/I) reductions. Moreover, the first cathodic process is responsible for the appearance, upon scan reversal, of an anodic wave at about -0.1 V.

The CV of the resulting adduct has two oxidations ($^{I}E_p^{ox} = 0.76$ V and $^{II}E_p^{ox} = 1.23$ V) and three reductions ($^{I}E_p^{red} \approx -0.88$ V, $^{II}E_p^{red} = -1.13$ V and $^{III}E_p^{red} = -1.71$ V).

The two anodic waves are probably centred at both Mo and V sites, and the shifts in the potentials upon adduct formation can be interpreted as for the above rhenium/molybdenum system.

With reference to the cathodic processes, the first and the second ones are probably centred at the V site (the presence of the above mentioned anodic wave, upon scan reversal after the first cathodic wave, as in the starting V complex, confirms that this wave is centred at the V site). In the adduct, the cathodic waves shift to slightly lower potentials than in the parent V complex, possibly as a result of the electron acceptance of this metal from the new cyanoimido-ligand. The third cathodic wave should be centred at Mo and is very similar to the reduction wave of the cyanoimido-complex conceivably for similar reasons to those presented above for the rhenium/molybdenum complex.

Conclusions

The relative electrochemical behaviour of the adducts reflects the electronic properties of the metal centres involved. Thus, in the trinuclear Pt adduct, the potentials of the redox processes centred at the Mo atom are very different from those in the bis(cyanoimide) complex, due to the strong σ-electron acceptor character of the Pt(II) atoms from the

cyanoimide ligands. In contrast, for both Re and V adducts, those redox processes occur at potentials which are similar to those in the parent complex, because Re(I) and V(III) also behave as π-electron donors to the NCN ligand.

The Pt(II) centre is a stronger Lewis acid than the Re(I) and V(III) sites, and the reduced and oxidized forms of the diadduct (which exhibits reversible redox waves) with the former Lewis acid are more stable than those of the monoadducts of the later ones (whose redox waves are irreversible).

References

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Acknowledgements