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Electrochemical behaviour of cyclometallated gold(III) complexes. Evidence of transcyclometallation in the fate of electroreduced species

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Abstract

The electrochemical behaviour of a series of neutral and cationic N–C and N–N–C cyclometallated gold(III) species: ([Au(py^1)(Cl)$_2$], Hpy^1 = 2-benzylpyridine; [Au(bipy^n)(Cl)][PF$_6$], Hbipy^1 = 6-benzyl-2,2′-bipyridine, Hbipy^2 = 6-(1-methylbenzyl)-2,2′-bipyridine, Hbipy^3 = 6-(1,1-dimethylbenzyl)-2,2′-bipyridine, Hbipy^4 = 6-phenyl-2,2′-bipyridine) has been investigated in different solvent systems using cyclic voltammetry and controlled-potential coulometry. All the species considered show, in cyclic voltammetry, an irreversible one-electron reduction in the potential range $-0.9/-1.2$ V versus Fc$^{+/0}$, using a Pt electrode. On the other hand, exhaustive coulometries have shown the consumption of a number of Faraday per mole within the range 1–2. The very complex decomposition of the electrogenerated species affords elemental gold and significant amounts of different gold by-products. In some situations (e.g. reduction of [Au(bipy^4)(Cl)][PF$_6$]), working with 0.1 mol dm^{-3} Na[PF$_6$], CH$_3$CN solvent system, it has been possible to characterise the most abundant gold(III) compound, by NMR, FAB-MS, and elemental analysis. The analytical and spectroscopic data provide evidence for the N–C bis-cyclometallated gold(III) derivative (e.g. [Au(bipy^4)$_2$][PF$_6$]); the result entails quite an unusual transcyclometallation process. The same compound can also be obtained, albeit in very minor yield, by chemical reduction of [Au(bipy^4)(Cl)][PF$_6$].

Keywords: Gold compounds; Cyclometallated species; Electrochemistry

1. Introduction

Despite the attention devoted recently to the chemistry of gold complexes [1], few articles deal with their electrochemical characterisation. One reason lies probably in the fact that it is usually difficult to obtain reproducible responses owing to poisoning adsorptions on the electrode.

The early published papers date back to the late 1970s: gold(III) complexes with porphirinic ligands were studied by Jamin and Iwamoto [2]: these compounds exhibit different redox processes when studied by cyclic voltammetry, actually involving the porphyrine system rather than the metal centre. In the subsequent years an extensive research has been performed by Van der Linden and co-workers [3–5], regarding the reduction of phosphine gold clusters. Finally, recent literature contributions deal both gold(I) and gold(III) complexes with chelate ligands bearing 'soft' donor atoms (sulphur and — mainly — phosphorus). In this connection, the studies of Laguna [6] have to be cited, referring on synthesis and characterisation by cyclic voltammetry of Au(II)–Au(I) dinuclear species with bridged diphenylphosphinoalkanes and pyridine-2-thiolates ligands, as well as those of Bjørnholm [7], referring on the voltammetric behaviour of Au(III) dithiolene complexes.

If the number of papers on the electrochemistry of gold complexes is relatively scarce, it is hard to find any articles at all dealing with organo–gold species. It is

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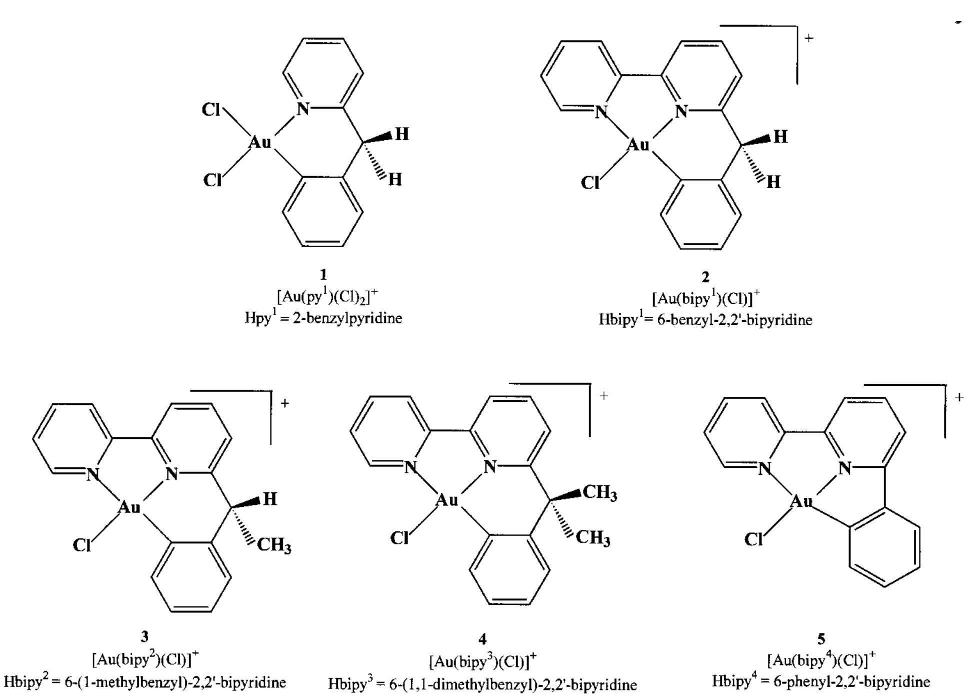

1
$[Au(py^1)(Cl)_2]^+$
Hpy^1 = 2-benzylpyridine

2
$[Au(bipy^1)(Cl)]^+$
$Hbipy^1$ = 6-benzyl-2,2'-bipyridine

3
$[Au(bipy^2)(Cl)]^+$
$Hbipy^2$ = 6-(1-methylbenzyl)-2,2'-bipyridine

4
$[Au(bipy^3)(Cl)]^+$
$Hbipy^3$ = 6-(1,1-dimethylbenzyl)-2,2'-bipyridine

5
$[Au(bipy^4)(Cl)]^+$
$Hbipy^4$ = 6-phenyl-2,2'-bipyridine

Scheme 1.

worth citing a paper on the voltammetric and polarographic behaviour of gold(I) species [8], and an article on the electrochemical behaviour of organo–gold(III) and gold(I) derivatives, with pentafluoro- and pentachlorophenyl ligands by Koelle and Laguna [9].

In the frame of a research devoted to synthesis, characterisation and reactivity of organometallic and coordination compounds of metal ions with d^8-configuration, bearing heterocyclic nitrogen-containing ligands [10,11], a study of the electrochemistry of the cyclometallated Au(III) species shown in Scheme 1 is reported here.

All complexes, except for the neutral compound **1**, are cationic species, hexafluorophosphate being the relevant counter-ion.

2. Experimental

2.1. Synthesis

Compounds **1**–**5** were prepared as reported elsewhere [12,13].

2.1.1. Chemical reduction of $[Au(bipy^4)Cl][PF_6]$

To $[Au(bipy^4)Cl][PF_6]$ (**5**), 60.9 mg (0.1 mmol) in 20 ml anhydrous MeOH, a 20 ml aliquot (0.123 mmol) of a solution containing 58.2 mg $NaBH_4$, in 250 ml anhydrous MeOH was added under inert Ar atmosphere. The colour of the suspension obtained changed from clear yellow to dark yellow. The mixture was allowed to react for 45 min at room temperature (r.t.), then filtered off, evaporated to dryness and washed three times with diethyl ether in order to separate the $Hbipy^4$ ligand. The crude solid was then crystallised from dichloromethane and diethyl ether to give a white compound (**6**, 3.8 mg). ^{1}H-NMR ($CDCl_3$, δ): 8.15 (d, 2H, H(6')). 7.26–8.07 (m, 20H). (CD_3COCD_3, δ) 7.38–7.56 (m, 8H), 7.87 (t, 2H), 8.06 (dd, 2H), 8.14 (d, 2H), 8.18–8.28 (m, 8H).

^{13}C-{^{1}H}-NMR (CD_3COCD_3, δ) 121.76, 123.50, 123.64, 127.22, 128.94, 129.25, 132.45, 135.04, 140.36, 142.19, 150.36 (aromatic CH), 144.54, 146.43, 154.30, 157.09, 160.24 (aromatic C). ^{31}P-{^{1}H}-NMR ($CDCl_3$, δ) 143.61 (m, PF_6^-).

2.2. Electrochemistry

All electrochemical experiments were performed using an Amel System 5000 computerised instrument. Cyclic voltammograms were recorded on a Hewlett–Packard model 7475A digital plotter, connected to the System 5000 via a suitable interface (Amel model 865 plotter adapter/converter). High scan rate tests were performed on a CHI model 650 computerised instrument, controlled by a Pentium II 350 MHz Personal Computer, running in Windows 98 environment. Cyclic voltammetric and controlled potential coulometric tests were carried out in conventional electrochemical cells, i.e. in an H-shaped cell in the latter case, the working electrode being separated from auxiliary and reference compartments by sintered glass disks. A cell with more rigorous geometrical requirements, necessary in order to minimise the ohmic drop between working and reference electrode, was used in high potential scan rate voltammetric experiments [14]. The working electrode was a platinum or a gold disk with a diameter of ca. 2 mm in the voltammetric tests and a large platinum gauze in the exhaustive electrolysis experiments. The reference electrode was an SCE, connected to the working electrode compartment through a salt bridge containing the same organic solvent medium. The auxiliary electrode was a mercury pool (or a Pt wire in high potential scan rate tests). In all the experiments positive-feedback IR drop was performed. Acetonitrile (CH_3CN), tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) solvents (all from Aldrich, anhydrous, 99+ %, Gold Label, water $<0.005\%$, packaged under nitrogen) were used without further purification. Tetraethylammonium hexafluorophosphate ($[Et_4N][PF_6]$), tetrabutylammonium hexafluorophosphate ($[n\text{-}Bu_4N][PF_6]$) and sodium hexafluorophosphate ($Na[PF_6]$) (Fluka, puriss., $>99\%$) supporting electrolytes were crystallised twice from methanol–diethyl ether, then stored under reduced pressure and dried overnight at 50°C below 500 Pa before use. Cyclic voltammetric and controlled potential coulometric tests have been carried out on solutions carefully de-aerated by bubbling 99.999% pure Ar through; the same gas flowed over the solution during the experiments. The tests have been performed at room temperature and the reported potential values are referred to *bis*-cyclopentadienyliron(III) | iron(II) couple ($Fc^{+/0}$, $E_{1/2,r} = +0.43$, $+0.46$ and $+0.55$ V versus SCE in MeCN, CH_2Cl_2 and THF solvent, respectively), used as internal reference. $E_{1/2,r}$, a good experimental approximation of the standard potential of the redox couple, was computed as half the sum of forward and directly associated backward peak potentials of the cyclic voltammetric responses [15,16].

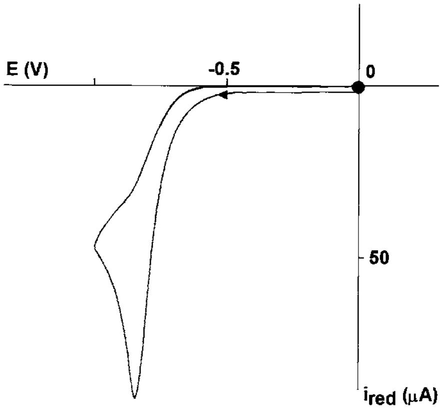

Fig. 1. Cyclic voltammetric curves recorded on a $1 \cdot 10^{-3}$ mol dm^{-3} compound **3**, 0.1 mol dm^{-3} $[Et_4N][PF_6]$, CH_3CN solution. Pt working electrode; 0.2 V s^{-1} potential scan rate; ● starting potential for the initially cathodic scans. *E* in V, is referred to as the $Fc^{+/o}$ couple; *i* in μA.

3. Results

3.1. Cyclic voltammetry of species **1–5**

Table 1 summarises the voltammetric data for species **1–5**, recorded in different solvents and supporting electrolytes, as indicated in the same Table.

All the species considered show on a platinum electrode, at a potential sweep rate of 0.20 V s^{-1}, a relatively easy and irreversible reduction in correspondence to a well reproducible voltammetric peak (see, for example, Fig. 1). For compounds **2–5**, in all the solvent media used, working at a potential sweep rate of 0.20 V s^{-1}, the peak potential is located within the narrow range $-0.9/-1.0$ V; only in the case of compound **1** the cathodic response is observed at a more negative value. Surprisingly, in all cases the location is slightly more cathodic when $Na[PF_6]$ is used as the supporting electrolyte.

Except for compound **1**, the $E_{p/2,c} - E_{p,c}$ values are between 60 and 90 mV in CH_3CN solvent, but notably higher in CH_2Cl_2, viz. in a medium with lower dielectric constant. The cathodic peak does not show any directly associated backward anodic response, even at potential sweep rates as high as 50 V s^{-1}; a 20 mV cathodic shift on the peak potential for a tenfold increase of the scan rate [16] is also observed for all compounds.

Working in 0.1 mol dm^{-3} $[Et_4N][PF_6]$, CH_3CN solvent, at cathodic potentials close to the breakdown of the supporting electrolyte, further ill defined cathodic peaks, rather low in height, are detected. These processes give rise to better defined responses when 0.3 mol dm^{-3} $[n\text{-}Bu_4N][PF_6]$, THF solvent medium is used, thanks to the enlarged cathodic potential window exhibited by this solvent medium.

Voltammetric studies performed with a gold electrode give responses strictly similar to those obtained with platinum, while no reproducible signal is recorded on mercury, possibly due to poisoning adsorption of the reduction product(s) on the electrode.

3.2. Controlled potential electrolysis and voltammetric characterisation of reduction products

Exhaustive coulometries have been performed in order to evaluate the number of electrons involved in the overall electrode process and to study the nature of the stable species formed in the solution. Different solvents (CH_3CN, CH_2Cl_2 or THF) and supporting electrolytes ($Na[PF_6]$, $[Et_4N][PF_6]$ or $[n\text{-}Bu_4N][PF_6]$) have been used, depending on the particular aspect to put in evidence. As an example, THF was chosen as a solvent

Table 1

Compound[a]	Solvent system[b]	Substrates			Reduced species		
		First cathodic process $E_{p,c}$ (V) (($E_{p,c/2}-E_{p,c}$) (mV))	Additional cathodic processes $E_{1/2}$ (V) or $E_{p,c}$ (V) ((ΔE_P, $E_{p,c/2}-E_{p,c}$) (mV))	Electronicity of the first cathodic process[c]	Cathodic processes $E_{1/2}$ (V) or $E_{p,c}$ (V) ((ΔE_P, $E_{p,c/2}-E_{p,c}$) (mV))	Anodic processes $E_{1/2}$ (V) or $E_{p,a}$ (V) ((ΔE_P, $E_{p,a}-E_{p,a/2}$) (mV))	Metallic Au recovered[d] %
1	a	−1.29 (170)		1.40	−1.98		58
	b	−1.19 (140)		1.50	−1.88	0.3; 0.53	48
2	a	−0.95 (80)	−1.53^{e}; −1.89^{e}	1.77	*−1.51* (100,80); −1.88	0.97	79
	b	−0.88 (90)	*−2.67* (110)^{e}	1.50	*−1.47* (50,90); *−2.63* (90,110); −1.60; −2.97	0.60	64
3	a	−0.98 (90)		1.52	*−1.51* (70,80); −1.93		59
	b	−0.93 (70)	*−2.68* (100)^{e}	1.43	*−1.49* (90,70); −1.89	0.37	42
	c	−0.97 (90)	−2.53^{e}; *−2.62* (160)^{e}	1.60	*−1.38* (90,80); −1.95; *−2.69* (140,130)	0.47; 0.87	49
	d	−0.95 (150)	−2.35^{e}	1.50	*−1.40* (80,80); −1.93	0.81; 1.51	30
	e	−0.95 (140)	*−1.43* (100)^{e}; −1.93^{e}	1.35	*−1.41* (140,80); −1.97	0.17; 0.82; 1.67	27
4	a	−0.97 (90)		1.60	*−1.57* (60,80); −1.90		49
	b	−0.91 (60)		2.00	*−1.45* (95,100); −1.79	0.37; 0.59; 1.10	69
5	a	−1.01 (80)	*−1.42* (60)^{e}; −1.86^{e}	1.50	*−1.42* (90,60); −1.85		50
	b	−0.96 (70)	−1.43^{e}	1.50	*−1.41* (100,60); −1.85	*0.49* (200,90); 1.57	44

[a] Pt is the working electrode. E in V, is referred to as the $Fc^{+/o}$ couple. Values in *italic*: $E_{1/2,r}$ for reversible or quasi-reversible reductions. Values underlined: $E_{p,c}$ ($E_{p,a}$) for irreversible reductions (oxidations). Potential scan rate, 0.2 V s^{-1}.

[b] (a) 0.1 mol dm^{-3} $Na[PF_6]$ supporting electrolyte in CH_3CN solvent; (b) 0.1 mol dm^{-3} $[Et_4N][PF_6]$ supporting electrolyte in CH_3CN solvent; (c) 0.3 mol dm^{-3} $[n\text{-}Bu_4N][PF_6]$ supporting electrolyte in THF solvent; (d) 0.3 mol dm^{-3} $[n\text{-}Bu_4N][PF_6]$ supporting electrolyte in CH_2Cl_2 solvent; (e) 0.3 mol dm^{-3} $[Et_4N][PF_6]$ supporting electrolyte in CH_2Cl_2 solvent.

[c] Value determined by exhaustive coulometry, expressed in Faraday mol^{-1}.

[d] Percentage of metallic gold recovered after exhaustive electrolysis, referred to the initial amount in the relevant compound.

[e] Ill defined or poorly resolved peak.

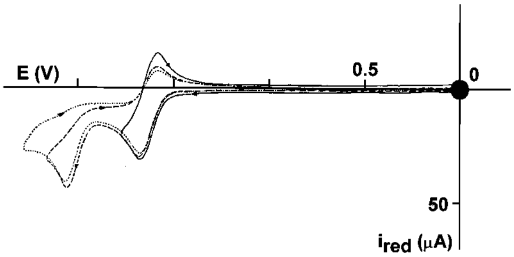

Fig. 2. Cyclic voltammetric curves recorded on a reduced solution of $1 \cdot 10^{-3}$ mol dm^{-3} compound **3**, 0.1 mol dm^{-3} Na[PF$_6$], CH$_3$CN solution. Pt working electrode; 0.2 V s^{-1} potential scan rate; ● starting potential for the initially cathodic scans, (—) first cycle; (---) second cycle; (···) third cycle. E in V, is referred to as the Fc$^{+/o}$ couple; i in μA.

with a particularly wide cathodic potential window, and CH$_2$Cl$_2$ when a low coordination capability was sought. For any possible combinations of solvent and electrolyte, repeated tests on each of compounds **1**–**5** led to the consumption of a number of Faraday per mole within the range 1–2. During the electrolysis the colour of the solution, initially yellow in the case of compounds **2**–**5**, faded, and a suspension of a dark solid formed. At the end of the electrolysis the working electrode was covered by a deposit that was either yellow and well adherent or dark brown and easy to take off. Cyclic voltammetric curves recorded on the reduced solutions of compounds **2**–**5** showed two cathodic processes undetectable in the starting solution. The less cathodic one is reversible, the relevant $E_{1/2,r}$ value being located between -1.4 and -1.5 V; the latter one is irreversible, with $E_{p,c}$ between -1.8 and -1.9 V. The height of the former peak never exceeds one half that of the first cathodic peak recorded on solutions of the starting compound. As an example, Fig. 2 reports cyclic voltammetric curves recorded on a reduced solution of $1 \cdot 10^{-3}$ mol dm^{-3} compound **3**, 0.1 mol dm^{-3} Na[PF$_6$], CH$_3$CN solution.

Further reductions are observed at much lower potentials, very close the solvent medium reduction, when THF is the solvent used and the electrolyte cation is an alkylammonium salt. By comparison with authentic samples, these signals can be ascribed to the reduction of the relevant Hbipy ligand.

In the case of compound **1** only one irreversible peak was detectable at the end of electrolysis, located between -1.9 and -2.0 V in dependence of the solvent system used.

Table 1 reports also the coulombometric results relative to the first reduction and the most significant voltammetric data for the reduced species afforded by electrolyses of compounds **1**–**5**.

3.3. Isolation and identification of the reduction products

The first step of isolation and identification of the reduction products consisted of a simple filtration that allowed the separation of the suspended solid, usually constituted by metal gold, as inferred from elemental analysis. In all cases in which Na[PF$_6$] was the electrolyte, NaCl, poorly soluble in all the solvents used, was recovered together to gold, accounting for 80–100% the chlorine present in the substrate. Accordingly, also when [Et$_4$N][PF$_6$] was the supporting electrolyte, chloride ions, no more bound to the metal, were present in the solution and detectable voltammetrically by a typical poorly reproducible, broad and irreversible anodic peak with $E_{p,a}$ at ca. $+0.6/+0.8$ V. Also in this case, the chloride could be quantified, through ionic chromatographic analyses, to an amount corresponding to 80–100% the total amount in the compounds **2**–**5**. We can hence conclude that in all cases the chloride ion is quantitatively released by the complex in the reduction process.

The amount of metallic Au recovered, in part as a deposit over the platinum working electrode and in part as a fine suspended solid is reported in Table 1. It is worth noting that the amount of metal is always in good agreement with the electronicity computed from the exhaustive electrolyses, assuming that gold which is not reduced to metal retains the initial oxidation state.

The separation of the soluble reduction products from the supporting electrolyte was performed by evaporation of the solvent followed by extraction of the reduced species with dichloromethane or benzene when using Na[PF$_6$] or [Et$_4$N][PF$_6$] as the supporting electrolyte, respectively. Evaporation of the solvent led to a solid, that was purified by several crystallisations from dichloromethane (or benzene)/diethyl ether and subsequently analysed preliminarily by thin layer chromatography (TLC) and then by ^{1}H and ^{31}P{^{1}H}-NMR spectroscopy. The residue is usually a mixture of many species; nevertheless, in the electrochemical reduction of compounds **2**, **4** and **5**, the high concentration of the most abundant compound has allowed us to achieve reliable structural information, mainly due to spectroscopic (^{1}H- and ^{31}P{^{1}H}-NMR), elemental analyses and FAB-MS techniques[1].

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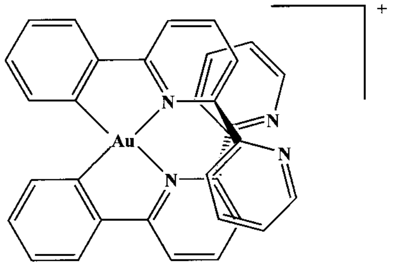
[1] Electrochemical reduction product of **2**: ^{1}H-NMR (CDCl$_3$, δ): 4.19, 4.30 (AB system, CH$_2$, 2H), $J_{AB} = 13.7$ Hz; 4.41, 5.12 (AB system, CH$_2$, 2H), $J_{AB} = 16.2$ Hz; 6.88–8.37 (m, aromatic protons, 22H); ^{31}P-{^{1}H}-NMR (CDCl$_3$, δ) 143.61 (m, PF$_6^-$); elemental analysis: Found: C 46.36; H 3.03; N 6.23%. C$_{34}$H$_{26}$N$_4$AuPF$_6$CH$_2$Cl$_2$ requires: C 45.82, H 3.08, N 6.11%. Electrochemical reduction product of **4**: ^{1}H-NMR (CDCl$_3$, δ): 1.88 (s, CH$_3$, 3H), 1.92 (s, CH$_3$, 3H), 1.93 (s, CH$_3$, 3H), 1.97 (s, CH$_3$, 3H); 6.84–8.73 (m, aromatic protons, 22H) ^{31}P-{^{1}H}-NMR (CDCl$_3$, δ) 143.61 (m, PF$_6^-$); elemental analysis: Found: C 45.22; H 3.79; N 5.44%. C$_{38}$H$_{34}$N$_4$-AuPF$_6$2CH$_2$Cl$_2$ requires: C 45.39, H 3.62, N 5.29%; FAB MS: m/z 743 [Au(bipy^3)$_2^+$]. Electrochemical reduction product of **5**: ^{1}H and ^{31}P-{^{1}H}-NMR: the spectrum is superimposable to that of **6** (see Section 2); elemental analysis: Found: C 44.47; H 3.10; N 6.64%. C$_{32}$H$_{22}$N$_4$AuPF$_6$CH$_2$Cl$_2$ requires: C 44.56, H 2.72, N 6.30%; FAB MS: m/z 659 [Au(bipy^4)$_2^+$].

4. Discussion

In view of the high electronegativity value of gold(III) [17] in comparison with other d^8 metal ions, it is not surprising that the first cathodic reduction of compounds **2**–**5** is much easier than for similar Pt(II) species [10,11], the difference being as high as 0.8 V. The peak potential is invariably located in the range from -0.9 to -1.0 V. Only the neutral species **1** shows a more negative reduction potential, likely owing both to 'electronic' (i.e. increased difficulty in reducing neutral than cationic species) and 'structural' (i.e. the decrease of the structural rigidity causes a cathodic shift of the reduction potential, as suggested by Warren and Bennett) [18] effects. The absence of any directly associated backward anodic response, even at potential sweep rates as high as 50 V s^{-1}, is consistent both with an irreversible charge transfer and with a charge transfer followed by a fast irreversible chemical reaction. Although our voltammetric findings can not give a definite answer about, the analysis of the voltammetric responses recorded at different scan rates tentatively suggests the occurrence of a quasi-reversible charge transfer which is strongly suspected to be followed by an irreversible reaction. This is supported by the observation that, at least in some cases, the irreversibility degree is not too high and is, however, coupled to the complete absence of any traces of associated backward responses. The not complete reversibility of the electron transfer is suggested by the values of $E_{(p/2,c)} - E_{p,c}$ (Table 1) and $\partial E_{p,c}/\partial \log v$; they always slightly exceed the reference values [16] (60 and 29.5 mV for a tenfold increase of scan rate, respectively) for a reversible, one-electron transfer.

The change of the supporting electrolyte slightly affects the location of the first reduction peak: it is always shifted towards more cathodic potentials when $Na[PF_6]$ is used in place of $[Et_4N][PF_6]$. It seems therefore that the organic electrolyte plays a role in the reduction mechanism of the substrates. However, no any reliable explanation can be given at the moment.



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Scheme 2.

By comparison with the height of the response of the $Fc^{+/0}$ redox couple, the electronicity of the first cathodic process on the voltammetric time scale can be estimated close to the unity for all the compounds; however, controlled potential electrolyses afforded electronicity values between 1 and 2 Faraday mol^{-1}. The occurrence of an ECE mechanism, where an irreversible chemical reaction is interposed between two subsequent electron transfers, is compatible with these results. Indeed, a comparison between the current peak before and after the electroreduction, suggests that the species obtained from exhaustive electrolysis is still a gold(III) derivative, present in the solution at a concentration equal to one half that of the starting complex. Although it is not easy to collect in all cases conclusive information about the exact nature of the complexes formed by reduction, mainly due to difficulties in the purification step, in the case of **2**, **4** and **5** and working with 0.1 mol dm^{-3} $Na[PF_6]$, CH_3CN solvent system, it has been possible to isolate a very little amount of the product to a purity degree sufficient to obtain reliable analytical results. FAB-MS findings show, (electroreduction of **4** and **5**), a molecular ion with mass corresponding to the relevant $[Au(bipy^n)_2]^+$ fragment. Also analytical data confirm an Au:bipy ratio of 1:2, while the $^{31}P\{^1H\}$-NMR spectroscopy reveals the presence of the PF_6^- anion. On the other hand, the ^1H-NMR spectra of the three species exhibit marked differences.

In particular, for compound afforded by electroreduction of **5**, the ^1H-NMR spectra show only one set of signals for the aromatic protons of the bipy moiety, indicating the equivalence of the two bipy units. The lacking of one aromatic proton per ligand (in comparison to the relevant $Hbipy^4$) and the marked shielding of the H(6′) proton (e.g. $\Delta\delta$ 0.5 ppm, with respect to free $Hbipy^4$) support the presence of a ligand N–C bound to the metal centre, and a not co-ordinating behaviour of the nitrogen of the external pyridinic ring. The shift to higher fields of the H(6′) proton may be due to its positioning in the shielding cone of one the aromatic rings present in the molecule.

On the whole the NMR spectra indicate a symmetric coordination of the two ligands around the metal.

In the case of **2** and **4**, the electrochemical reduction products show less simple ^1H-NMR spectra. Probably due to the presence of six-membered boat-like N–C cyclometallated rings, the two bipy units on the same metal atom are no more equivalent, as shown by the two AB systems for the CH_2 protons, in the case of the reduced product of **2**, and by the four singlets for the methyl groups in the case of reduced species of **4**. In agreement, two sets of signals appear in the aromatic.

In order to check the nature of the products obtained electrochemically, the substrates were reduced chemically by $NaBH_4$. The reaction was successful in the case of species **5**, leading to the same compound formed by electrode reduction, i.e. to complex **6** (see Scheme 2). This species was also characterised by $^{13}C\{^1H\}$-NMR spectroscopy: 16 lines are present in the aromatic region, assignable to 11 CH and five quaternary carbon atoms (per bipy unit), as indicated by an attached proton test (APT) experiment.

A *cisoid* disposition of the ligands is most probable, since usually observed in N–C bis-cyclometallated derivatives of d^8 metal ions [19]. Although the formation of species of this type is not favoured, being sterically crowded, they are not unprecedented, as reported, for example, by von Zelewsky et al. in the case of Pt complexes with 2,6-diphenylpyridine [20,21].

The electrode mechanism should hence be a very complex and quite unusual one, only roughly accounted for by the ECE scheme, seemingly involving also a *trans*-cyclometallation. The overall stoichiometry should be as follows:

$$2\ [\mathrm{Au(N{-}N{-}C)Cl}]^+ + 3e^- \rightarrow cis\text{-}[\mathrm{Au(N{-}C)_2}]^+ + \mathrm{Au}^0 + 2\ \mathrm{Cl}^-$$

where N–N–C and N–C indicate a three co-ordinate and a two co-ordinate C-deprotonated bipyridine, respectively.

Taking into consideration the whole of the results obtained, some hints on the reduction process can be drawn out. It has been already shown that the first step consists of a quasi-reversible one-electron charge transfer, the species produced being very short-lived ones. The reaction this species undergoes can be supposed to be a second order irreversible chemical reaction leading to a binuclear complex, likely to be a requirement to the occurrence of the subsequent transcyclometallation reaction. We can hypothesise that the dinuclear compound forms through an intermediate species; for example, this could be either a neutral species, obtained by coupling two $[\mathrm{Au(bipy^n)(Cl)}]$ reduced moieties, with subsequent release of one pyridine co-ordinating N atom from each metal centre, or a two-charged species like $[\mathrm{Au(bipy^n)}]_2^{2+}$, where bipy still acts like a terdentate ligand, both Cl^- ions being lost. Subsequently, independently from the actual nature of the intermediate, a further, easier, reduction (one additional electron per metal ion), with subsequent transcyclometallation, could lead to the Au(III) monomer, $[\mathrm{Au(bipy^n)_2}]^+$ and to metal Au. Finally, we wish again alert that this results are referred only to species afforded by electroreduction with 0.1 mol dm^{-3} $\mathrm{Na[PF_6]}$, $\mathrm{CH_3CN}$ solvent system, where the purification step is more efficient. For this reason, we cannot rule out, at the moment, the formation of such species also in the other solvent system.

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