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Bridging-ligand-facilitated intramolecular communication in homo- and heterobimetallic transition metal complexes of copper(I) and silver(I) as evidenced by cyclic voltammetry

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Abstract The electronic interaction between homo- and heterotransition metals of Group 11 in bimetallic complexes of the type $[(R_3P)M \leftarrow NN \rightarrow M'(R_3P)](X)_2$ ($R = C_6H_4CH_2NMe_2-2$; $M = M'$, $M \neq M'$, $M = Cu$, $M' = Ag$; $NN = NC_5H_4CN-4$, $1,4-(CN)_2C_6H_4$, $4,4'$ -bipy; $X = ClO_4$, OTf , PF_6), employing phosphanes as chelating ligands at the metal centers and various symmetric as well as asymmetric complexing molecules as bridging ligands between M and M' , has been studied by cyclic voltammetry. Based on the shift of the reduction potentials of the metal atoms, various degrees of intramolecular electronic communication have been identified. They are correlated with the type, the symmetry and the molecular structure of the bridging ligand.

Keywords Bimetallic complexes · Silver complexes · Copper complexes · Bridging ligands · Intramolecular communication

Introduction

Recently, the use of bis(alkynyl)titanocenes $[(\eta^5-C_5H_4SiMe_3)_2Ti(C \equiv CR)_2]$, $R =$ singly bound organic or organometallic group] as organometallic chelating ligands to stabilize, for example, low-valent mononuclear copper(I) or silver(I) salts has been reported ([1] and references therein). Such heterobimetallic $[(\eta^5-C_5H_4SiMe_3)_2Ti(C \equiv CR)_2]M$ species ($M = Cu, Ag$) can be spanned by various halides; their electrochemical behavior, in particular the influence of bridging halides,

has been described elsewhere [2]. The observed shifts of the reduction potentials of the irreversible electroreduction of the singly charged central ion M or M' (as a result of the reduction the metal M, M' is irreversibly expelled from the organometallic π -tweezer) were explained, taking into account the size, charge density and polarizability of both the coordinating halide bridge and the metal ion, which in turn also influence the degree of covalence of the metal-halide-metal ($M \leftarrow X \rightarrow M$) interaction. Intramolecular interactions (communication), evident from the position and multiplicity of the reduction peaks, have been reviewed using previously discussed concepts of intramolecular interaction and their classification [3] as a starting point. This classification, based essentially upon the strength and symmetry of ligand fields, was developed originally for crystalline mixed valence complexes wherein a given metal ion exists in different oxidation states. Various experimentally observable properties like, for example, optical absorptions caused by electron transitions between these ions or clearly different spectral properties (in IR, UV-vis or Mössbauer spectra), attributable to the different ions, have been used to define the following classes:

- I. Ions are in considerably different crystallographic environments; they can be clearly distinguished.
- II. Some delocalization, as with class III, takes place, but the ions are still distinguishable.
- III. Ions of different states of oxidation are on essentially the same equivalent sites; spectra of different ions cannot be distinguished.

Transposed to the molecular systems investigated here and invoking the concept of electronic communication (which is essentially effective also in the original concept without being called so explicitly), the classification would be:

- I. No communication between two metal ions; redox processes occurring at one ion do not influence the behaviour (e.g. the redox potential) of the other ion.

Dedicated to Prof. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry

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- II. Intermediate case, e.g. manifest in broadening of a reduction wave of a binuclear homometallic complex without clear separation of reduction waves.
- III. Strong communication, e.g. reduction of one ion causes a significant shift of the reduction potential of the other ion.

To our knowledge, this classification has not been applied to multinuclear homo- and heterometallic organometallic complexes so far.

Changing from the organometallic π -tweezers to, for example, multipodal phosphanes such as $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_3$, also allows the synthesis of copper(I) or silver(I) species, which are stabilized in their mononuclear state by the donor atoms P and N (Leschke M, Lang H, Holze R, submitted for publication). The latter molecules are of interest, since they can be used as CVD precursors, as catalysts in homogeneous catalysis or as model compounds to study intramolecular electron transfer processes.

In this report we present the results of cyclic voltammetric studies of various homo- and heterobimetallic copper(I) and silver(I) complexes with the stabilizing phosphane ligand $\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_3$ attached to the metal ions and bridging nitrogen-containing ligands. The simplified molecular structures of the investigate complexes are depicted in Fig. 1. The various types of ligand, their symmetry [identical anchoring sites (see e.g. **2**, **3**) or different anchoring sites (see e.g. **1**)] and their capability of providing possibilities of internal charge delocalization within conjugated systems provide a considerable range of conceivable degrees of electronic communication. In a companion paper we describe electrochemical properties and structure-reactivity relationships of the corresponding monometallic complexes (Leschke M, Lang H, Holze R, submitted for publication). Details of the structure as derived from X-ray structure analysis and various spectroscopic studies applied to the investigated compounds, both in the solid and the dissolved states, are reported elsewhere [4, 5].

Experimental

The preparation and extensive characterization of the copper and silver complexes depicted in Fig. 1 have been reported elsewhere [4, 5]. Essentially, these complexes were synthesized by reacting two moles of the phosphane-stabilized metal complexes (as perchlorate, tetrafluoroborate or triflate salts) with one mole of the bidentate ligand NN.

Cyclic voltammograms (CVs) were recorded in a dried cell purged with purified argon. Tetrahydrofuran used as the electrolyte solvent was purified according to standard procedures [6] and used immediately after being freshly distilled. $[n\text{-Bu}_4][\text{PF}_6]$ dried in an oil pump vacuum at 120 °C was added as supporting electrolyte at a concentration of 0.1 M. Compounds under investigation were added at 1 mM concentration. A platinum disc served as working electrode; a platinum wire was used as counter electrode. A saturated calomel electrode in a separate compartment served as reference electrode; for ease of comparison, all electrode potentials are

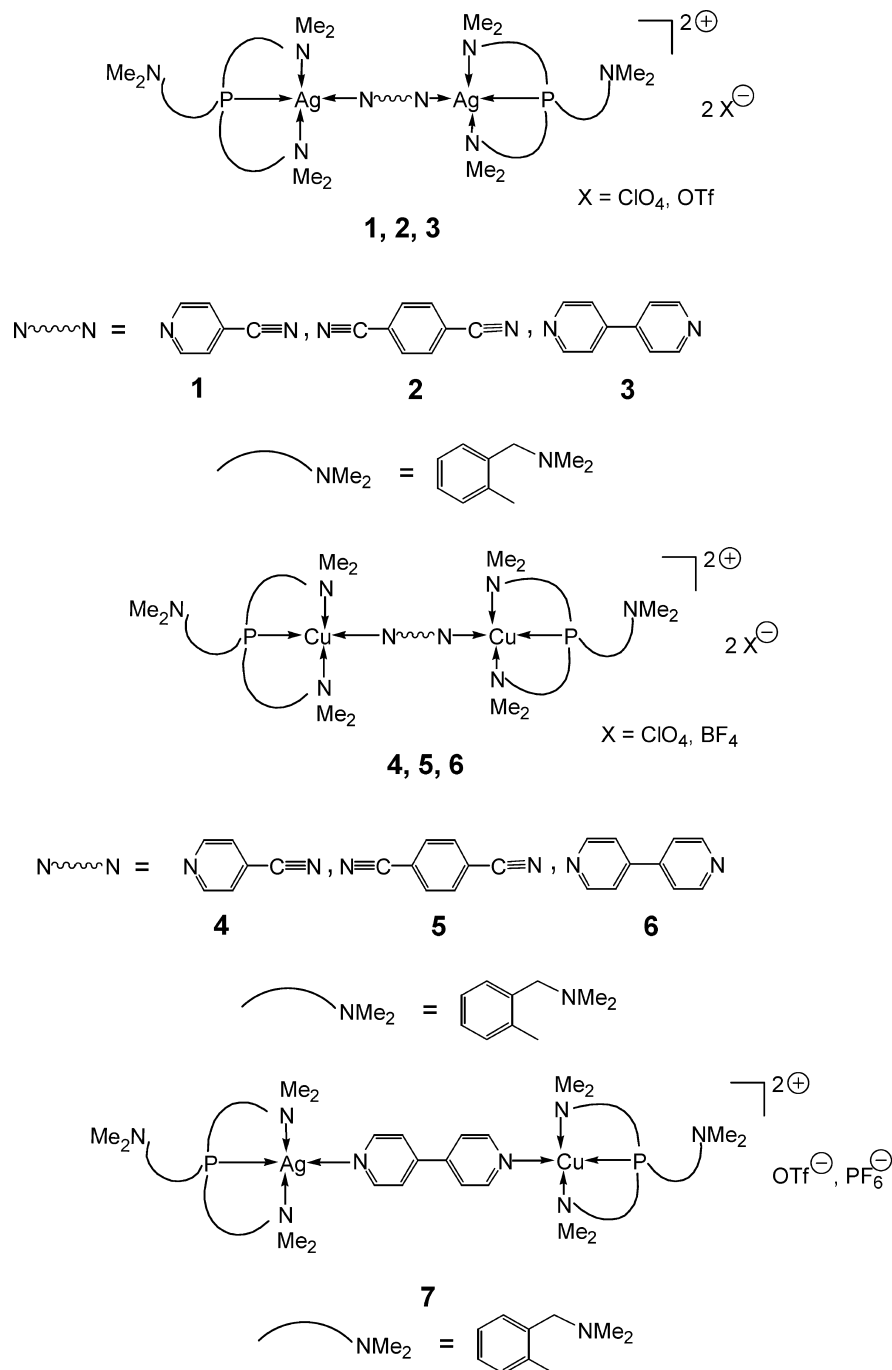
converted using the redox potential of the ferrocene/ferrocinium couple as reference ($E_{\text{FeC}} = 0$ mV) [7]. CVs were recorded at a scan rate of 0.1 V s^{-1} using a Voltalab 3.1 potentiostat (Radiometer) equipped with a digital electrochemical analyser DEA 101 and an electrochemical interface IMT 102. All experiments were run at room temperature (25 °C).

Results and discussion

A CV of the homobimetallic silver(I) complex **1** shows two reduction peaks with no corresponding oxidation peak (Fig. 2). Reduction of the silver ion results obviously in fragmentation of the species; after reduction of the first silver ion at $E_{\text{red,FeC}} = -1.37 \text{ V}$, the first phosphane ligand is released; the 4-cyanopyridine remains coordinated to the second silver ion in such a way that the sp^2 hybridized nitrogen atom of the pyridine unit is datively bound to silver(I), which is the most likely coordination of the 4-cyanopyridine group to a transition metal (Al-Anber M, Rheinwald G, Lang H, in preparation; [8]). This ion, $[\{\text{P}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}2)_3\}\text{Ag}(\text{NC}_5\text{H}_4\text{CN-}4)]^+$, is reduced at the second peak at $E_{\text{red,FeC}} = -1.91 \text{ V}$, resulting once more in the release of a phosphane ligand, a silver atom and the 4-cyanopyridine molecule (for a listing of all relevant data, see Table 1). Confusion of any of these peaks with reduction peaks caused by the phosphane or the 4-cyanopyridine ligand is unlikely; available data pertaining to redox processes of the ligands [9] are also listed in Table 1. Data on the electro-reduction of cyanopyridines are available only for aqueous solutions of various pH values, as reviewed by Lund and Hammerich [10]. Assignment of the reduction peaks to the silver ions being in a chemically different environment is possible when taking into account the different coordinating properties and electronic charge donating capabilities of the nitrile nitrogen and the pyridine nitrogen atoms. The former is a less strongly interacting one; consequently the silver ion with the attached nitrile group is more prone to reduction: it is reduced first.

This suggestion can be tested by considering the CV of complex **2**. Both silver ions are coordinated by a nitrile nitrogen, but only one reduction peak (once more without a corresponding oxidation peak) appears at $E_{\text{red,FeC}} = -1.31 \text{ V}$ (see Fig. 3). The small difference to the value found with **1** may indicate a slightly different charge distribution; the somewhat broad shape of the peaks makes such an interpretation only tentative. The redox peak of the ligand (a thorough comparative study of numerous nitrogen-containing ligands, including those employed here, is currently under way; the results will be reported in due course [9]; preliminary evidence as shown in Fig. 3 supports the statement provided above) as shown also in Fig. 3 is located far away from the reduction peak of the silver ions. Because reduction of the silver ions results in complete fragmentation of the bimetallic complex, no speculation about intramolecular electronic communication is reasonable; instead, it

Fig. 1 Simplified structural formulas of the investigated complexes 1–7



seems safe to say that both silver ions behave totally independently.

In compound **3**, both silver ions are spanned by 4,4'-bipyridine (see Fig. 4). The observed single reduction peak at $E_{\text{red,FeC}} = -1.33$ V seems to be at first glance in contradiction to the interpretation of the behavior of **1**, because both silver ions are coordinated with a pyridine nitrogen which in **1** resulted in a reduction peak at $E_{\text{red,FeC}} = -1.91$ V. The difference between the value found here and the value found with **1** can be rationalized in part when taking into account that, in **3**, essentially only a single pyridine unit is coordinated with the

silver ion whereas in **1** the whole 4-cyanopyridine unit is interacting with the second silver ion after the first silver ion has been split off. In addition, both silver ions are slightly out of the plane with the pyridine ring systems, further hindering electronic communication. In **1** the 4-cyanopyridine is coordinated with the sole remaining silver ion; thus a considerably larger charge transfer has to be assumed. The two additional redox peaks observed at significantly more negative electrode potentials in Fig. 4 are caused by reversible redox processes of the 4,4'-bipyridine. The values correspond closely to those reported by Rusina et al. [11] for related bipyridines.

Fig. 2 Cyclic voltammogram (CV) of complex **1**

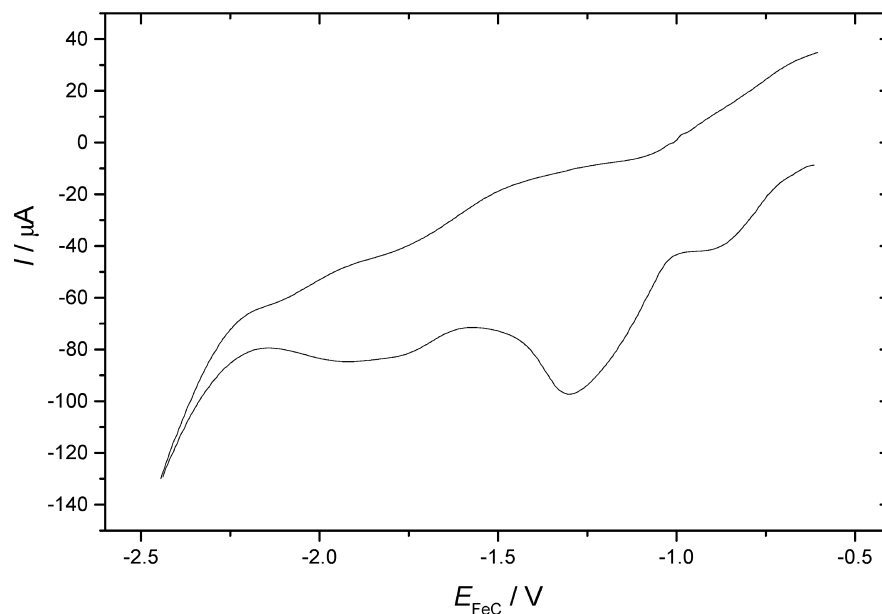


Table 1 Data from CVs of the investigated complexes 1–7

Complex ^{a,b}	Figure	$E_{\text{red,FeC,Ag(I)/Ag(0)}} \text{ (V)}$	$E_{\text{red,FeC,Cu(I)/Cu(0)}} \text{ (V)}$	$E_{0,\text{FeC,Cu(I)/Cu(II)}} \text{ (V)}$	$E_{0,\text{Lig}} \text{ (V)}$
1 [(R ₃ P)Ag-NC ₅ H ₄ -CN-4-Ag(PR ₃) ²⁺	2	-1.37 -1.91	–	–	-2.46 [11] ^c
2 [(R ₃ P)Ag-NC-C ₆ H ₄ -CN-Ag(PR ₃) ²⁺	3	-1.31	–	–	-2.16
3 [(R ₃ P)Ag-bipy-Ag(PR ₃) ²⁺	4	-1.33	–	–	-2.57 -2.94
4 [(R ₃ P)Cu-NC ₅ H ₄ -CN-4-Cu(PR ₃) ²⁺	5	–	-1.48 -1.94	0.07 -0.38	-2.46 [11] ^c
5 [(R ₃ P)Cu-NC-C ₆ H ₄ -CN-Cu(PR ₃) ²⁺	6	–	-1.77	-0.43	-2.16
6 [(R ₃ P)Cu-bipy-Cu(PR ₃) ²⁺	7	–	-1.74	-0.44	-2.57 -2.94
7 [(R ₃ P)Ag-bipy-Cu(PR ₃) ²⁺	8	-1.41	-1.83	-0.41	-2.57 -2.94

^aR = C₆H₄CH₂NMe₂-2; counter ion = OTf⁻, ClO₄⁻ and/or PF₆⁻

^bbipy = 4,4'-bipyridine; NC-C₆H₄-CN = 1,4-(CN)₂C₆H₄; NC₅H₄-CN-4 = 4-cyanopyridine

^cSee text for further explanation

Fig. 3 CV of complex **2** (solid line); CV of the ligand NC-C₆H₄-CN (dotted line)

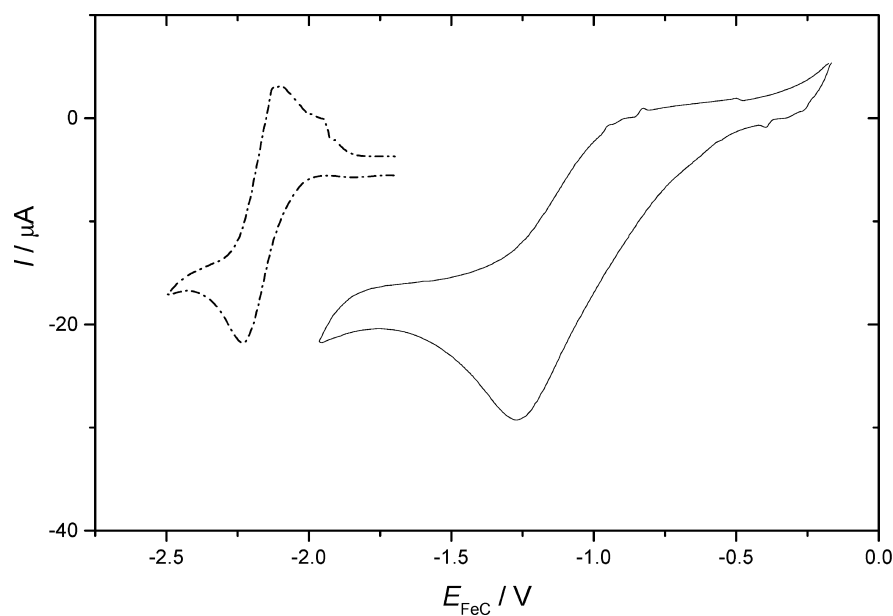


Fig. 4 CV of complex 3

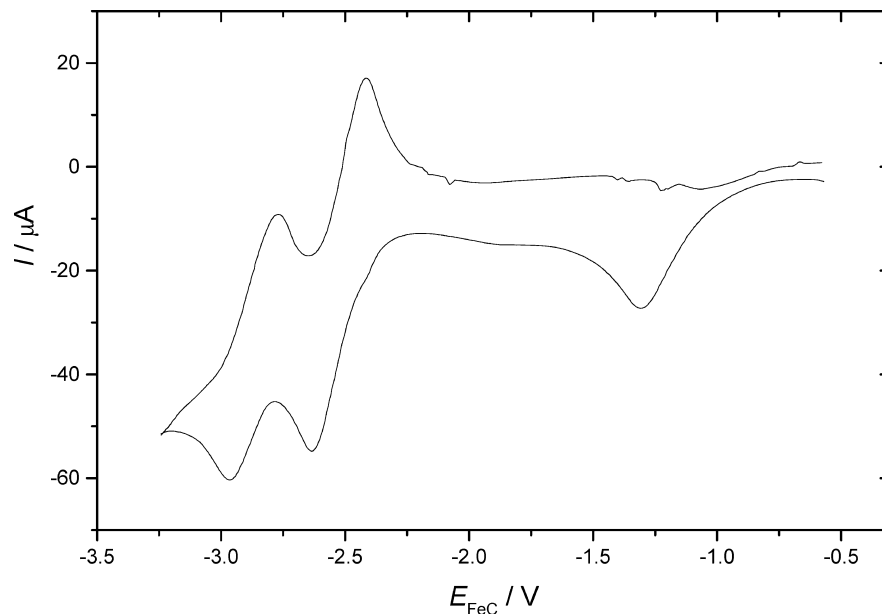
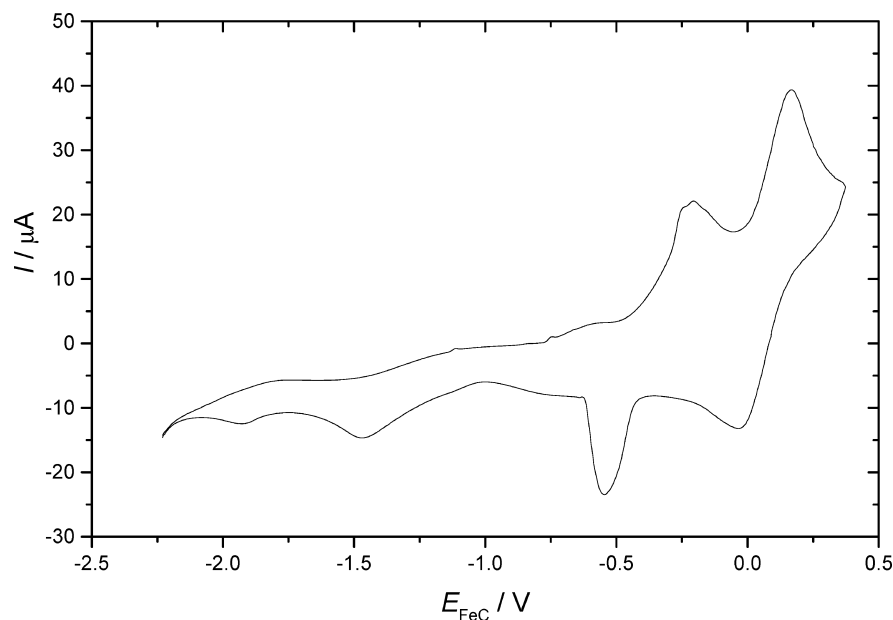


Fig. 5 CV of complex 4



The results obtained with the copper complexes **4–6** are basically similar (see Figs. 5, 6, 7); the explanation of the observed number and position of the reduction peaks follows essentially the same lines of reasoning. Somewhat surprising is the fact that the first reduction wave, which was located in a fairly narrow range with the silver complexes **1–3**, is spread over a much larger range in case of the homobimetallic copper analogues **4–6**. Unfortunately, support for any conceivable explanation cannot be obtained from, for example, structural data (X-ray crystallography) of these compounds since no single crystals could be prepared [4]. IR data for **4** and **5** showed a similar shift of the CN stretching band, indicative of some electron transfer. An explanation of

the shift of the reduction potential of the nitrile-coordinated copper ion by about 300 mV from **4** to **5** also cannot be obtained from CVs of the mononuclear phosphane-stabilized copper complex with a 4-cyanopyridine group [12]. Because of the stronger coordinating capability of the pyridine nitrogen atom, the latter nitrogen will always be the anchoring site towards the metal [8].

Based on current knowledge and by comparison with the respective silver complexes (*vide supra*), it may be suggested that the smaller copper ion (as compared to silver), with a consequently higher charge density, receives more charge from the nitrile nitrogen atom in case of **4** with the asymmetric 4-cyanopyridine than with **5**,

Fig. 6 CV of complex 5

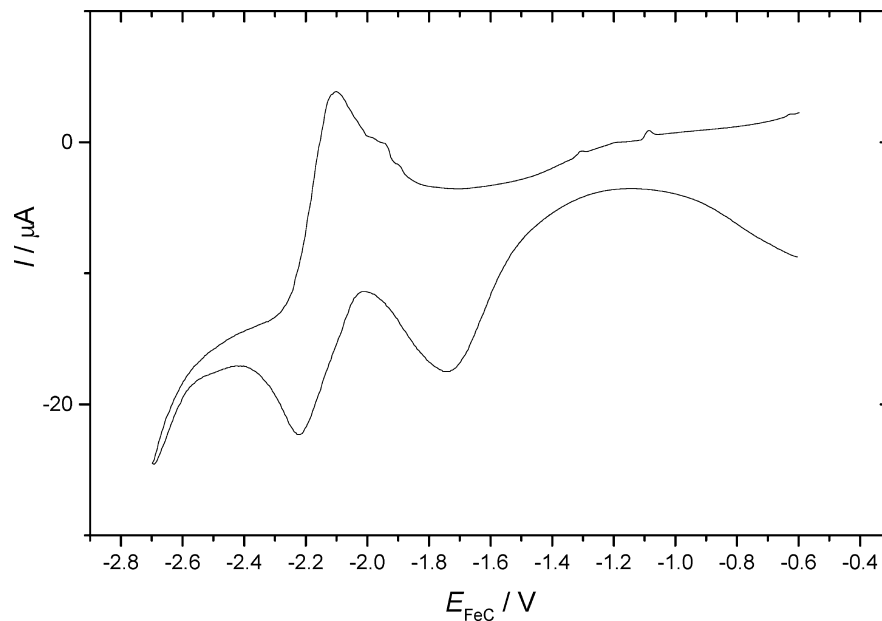
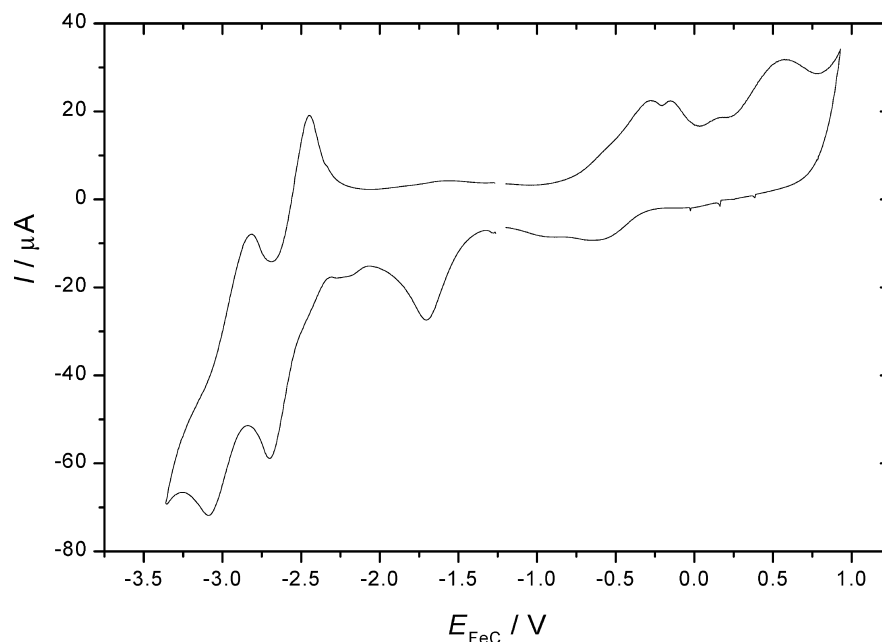


Fig. 7 CV of complex 6



where the ligand (having two nitrile substituents) has to interact with two copper ions. The single reduction wave in **4** and **5** is considerably closer to the second wave in **4** and supports this assumed property of the copper ion. The copper-containing complexes **4–6** show a copper(I)/(II) redox couple, which is reversible [in contrast to copper(I) reduction]. The positions of the first and second oxidation waves in the case of **4** with an asymmetric bridging ligand and the positions of the single peaks with **5** and **6** can be explained by invoking similar arguments as used earlier.

Of course, the copper ion interacting with the stronger electron donor (the pyridine nitrogen atom) will be

reduced first in **4**. The distance from the second oxidation peak is very similar to the values reported for the distance of the reduction peaks. The position of the single redox peak pair of **5** and **6** causes some ambiguity. Taking only **6**, the value is very close to the value of the corresponding first redox potential of **4**; both are assigned to a redox process involving a pyridine-nitrogen-coordinated copper ion. The value of the redox potential in **5** is practically the same, although both copper ions are interacting with nitrile nitrogen atoms. Perhaps, as suggested above, the particular properties of the copper ion mask in part the different properties of the nitrogen ligand sites involved here.

Fig. 8 CV of complex 7

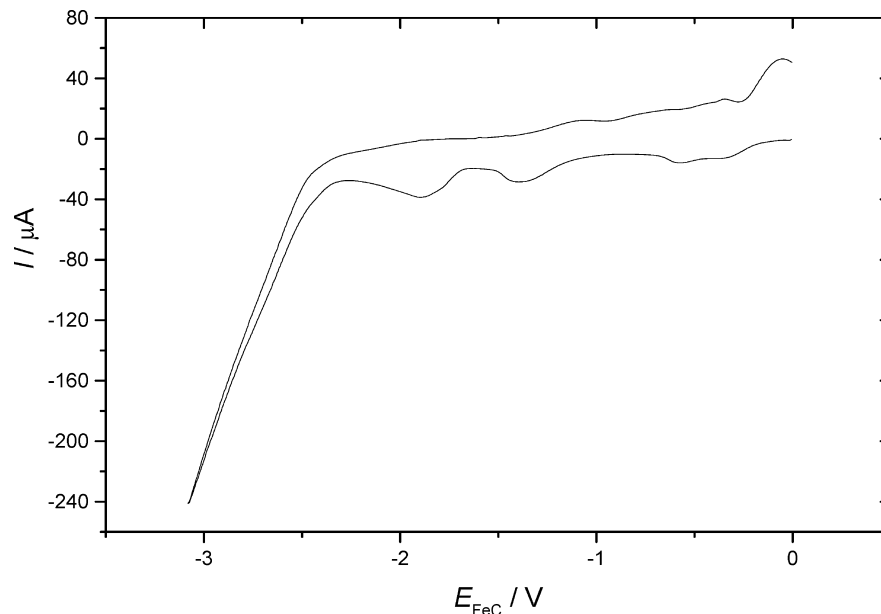


Figure 8 shows a CV of the heterobimetallic complex **7**. The first reduction peak at $E_{\text{red,FeC}} = -1.41$ V is assigned to the irreversible reduction of the silver ion. It is slightly shifted to more cathodic values in comparison to the homobimetallic silver complex **3**. In the absence of further structural information, no reliable explanation can be provided. This shift might be indicative of a larger contribution of a resonance structure of the 4,4'-bipyridine ligand with a negative charge located on the nitrogens and the bridging bond between the pyridine units showing some double bond character. The absence of any twisting of this bond found with **3** supports this assumption. Thus, this molecule might be classified, in analogy to the classification scheme for mixed valency compounds proposed by Robin and Day [3], as a class II system.

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