Electronic Interactions in Copper(I)- and Silver(I)-Complexes between the Ligands and Metals as Evidenced with Cyclic Voltammetry

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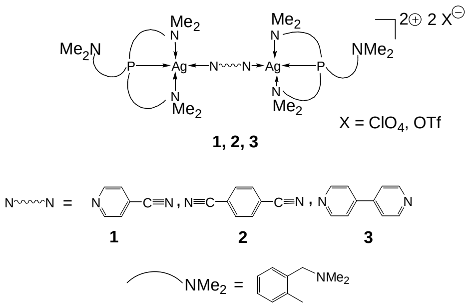
Introduction

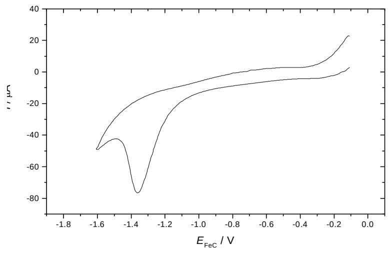
Recently the use of bis(alkynyl)titanocenes ($((\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CR)_2$, R = singly bound organic or organometallic group) as organometallic chelating ligands to stabilize e.g. low valent mononuclear copper(I) or silver(I) salts has been reported[1]. Such heterobimetallic $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CR)_2]M$ species (M = Cu, Ag) can be spanned by various halides; their electrochemical behavior, in particular the influence of bridging halide ligands, has been described elsewhere[2]. Observed shifts of 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 M←X→M interaction. Changing from the organometallic π-tweezers to e.g. multipodale phosphanes, such as $P(C_6H_4CH_2NMe_2\text{-}2)_3$, also allows the synthesis of copper(I) or silver(I) species[3], which are stabilized in their mononuclear state by the donor atoms P and N. 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.

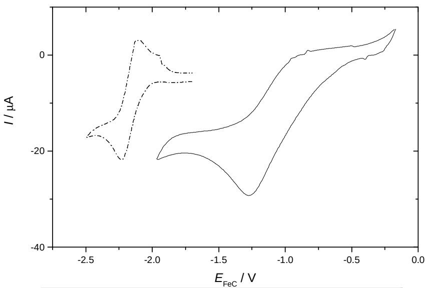
Experimental

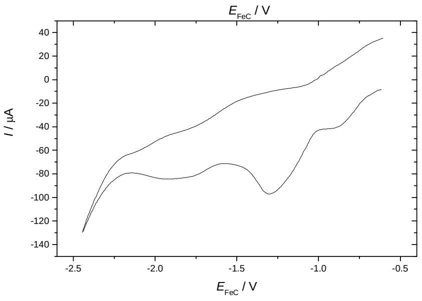
Preparation and extensive characterization of the mono- and bimetallic copper and silver complexes as depicted in Fig. 1 (as typical example the homobimetallic silver complexes are shown) have been reported elsewhere[4].



Results and Discussion







CVs always recorded in the negative going direction revealed a single reduction peak or two reduction peaks depending on the number of metal ions and the intramolecular interaction. The following example shows a typical CV of a mononuclear silver complex with a 2,2'-bipyridyl ligand. Upon reduction the silver atom is removed, the complex fragmented. With binuclear complexes one reduction wave is observed when the metal ions are in chemically identical environments without any intramolecular communication taking place which might influence the second reduction process (see left). The additional redox peak pair is caused by the 1,4-dicyanobenzene ligand spanning the silver ions. When the metal ions are in different environments different reduction potentials are observed (see left). The spanning ligand between the silver ions is 4-cyanopyridine. As the reduction of the silver and copper ions always results in fragmentation identification of intramolecular interaction and thus assignment to the classes of mixed valence compounds proposed by Robin and Day[5] is impossible. This is different with respect to the reversible Cu(I)/Cu(II) redox pair. No fragmentation occurs. In case of the binuclear copper complexes with symmetrical bridging ligand (4,4'-bipyridine and 1,4-dicyanobenzen) only one reduction peak was found, i.e. no electronic interaction (class I), in case of the asymmetric copper complex with the bridging 4-cyanopyridine two peaks were found because of the different coordinating capabilities of the nitrile and the pyridine nitrogen.

In case of the heterobimetallic complex with a bridging 4,4'-bipyridine unit shifts of the reduction potentials of the metal ions as compared to the homobimetallic complexes were found indicative of class (II) complexes.

Acknowledgments

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References

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