Electron Transfer Studies in trans-Platinum Bis(Acetylide) Complexes

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Introduction

Compounds with two redox-active transition metal fragments connected via carbon-rich \(\pi\)-conjugated spacer units have received considerable attention as they can be used for electron transfer studies and can be regarded as model compounds for molecular wires.\(^1\) Herein, we report on the synthesis and characterization of trans-platinum bis(acetylide) complexes containing ferroceny1 units as well as their electrochemical and spectro-electrochemical behavior. Furthermore, the influence of the ferroceny1 substituents of the phosphines on the intercalation charge-transfer will be discussed.

Synthesis of trans-Platinum Bis(Acetylide) Complexes

The synthesis of the trans-platinum bis(acetylides) \(5a\) and \(5b\) is presented in Scheme 1. Reaction of two equivalents of the ferroceny1 phosphines \(1a\) and \(1b\) with \([\text{PtCl}_2(\text{SEt})_2]\) produced the platinum(II) chlorides \(3a\) and \(3b\) as orange colored solids. Complexes \(5a\) and \(5b\) were prepared by treatment of \(3a\) and \(3b\) with two equivalents of cuprous ferrocenylacetylide in pyridine at 70 °C.

![Scheme 1. Synthesis of trans-platinum bis(acetylides) complexes 5a and 5b.](Image)

Electrochemistry

The redox properties of compounds \(3a, 3b\) and \(5a - 5c\) have been studied by cyclic voltammetry and were compared with the electrochemical behavior of the literature known complex trans-[Pt(C=C-C_F)P(Bu)_3] \({}^2\) \((6c)\). As supporting electrolyte 0.1 mol/L solutions of \([N\text{Bu}_4][B(C_6F_5)_4]_2\) in dichloromethane were used.

Figure 1. Cyclic voltammograms of complexes \(3a\) and \(3b\).

Figure 2. Cyclic voltammograms of complexes \(5a - 5c\).

Compounds \(5a - 5c\) show one reversible redox process for each ferrocenyl unit. By comparison with complex \(5c\) the first two processes can be assigned to the ethynylferrocenyl groups. In complexes \(5a\) and \(5b\) two and four, respectively, further redox processes at higher potentials can be observed for the ferroceny1 units bonded to the phosphorus atoms. Moreover, the peak separation \(\Delta E_{\text{p}}\) for the first two processes increases from \(5c\) (107 mV) to \(5a\) (116 mV) to \(5b\) (120 mV) with an increasing number of ferroceny1 units present in the phosphines. The results of the electrochemical investigations are an indication for weakly coupled II systems according to Robin and Day.

Conclusion

A series of trans-platinum bis(acetylides) were synthesized and the electronic coupling between the terminated redox-active units was studied. Electrochemical investigations indicated electronic communication between the ethynylferrocenyl units. The results were confirmed by in situ UV/Vis-NIR measurements. No intercalation charge-transfer band could be observed for the phosphine bonded ferroceny1 groups, while a small interaction between the ethynylferrocenyl groups exists. Furthermore, it could be shown that the phosphines influence the interaction between the ethynylferrocenyl units. An increasing donor ability of the phosphines results in an increased electronic communication.

Spectro-Electrochemistry

The spectro-electrochemical measurements were performed in an OTTLE (Optically Transparent Thin Layer Electrode) cell by stepwise increasing the potentials from -100 to 1300 mV that contained dichloromethane solutions of complexes \(3a, 3b, 5a\) and \(5b\) (1.0 mM) and \([N\text{Bu}_4][B(C_6F_5)_4]_2\) (0.1 M) as supporting electrolyte.

![Figure 3. NIR spectra of 3a (left) and 3b (right) at rising potentials (3a: -100 to 1300 mV, 3b: -200 to 1200 mV vs Ag/AgCl).](Image)

![Figure 4. Left: NIR spectra of 5a at rising potentials (bottom: 0 – 500 mV, top: 500 – 1200 mV vs Ag/AgCl); right: NIR spectra of 5b at rising potentials (bottom: 250 – 450 mV, top: 450 – 1200 mV vs Ag/AgCl).](Image)

Molecules \(5a\) and \(5b\) show one absorption during the oxidation, which steadily increases and a second absorption, which decreases after reaching a maximum at 500 mV \((5a)\) and 450 mV \((5b)\), respectively. After deconvolution, the first absorption at 1000 nm can be assigned to a ligand-to-metal charge-transfer and the second at 1200 – 1400 nm to an intercalation charge-transfer process. On account of the small intensities \((5a: 293 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}, 5b: 324 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})\) and the large bandwidth-at-half-height values of the ICT absorption \((-2500 \text{ cm}^{-1}\)) a classification in weakly coupled II systems according to Robin and Day can be made. Furthermore, it could be shown that an increasing number of ferroceny1 units bonded on phosphorus (decreased donor properties) resulted in a decreasing electronic coupling between the ethynylferrocenyl groups.

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