Introduction

Recently, a series of multiferrrocenyl-functionalized five-membered heterocycles including turan, thiophene and pyrrole has been prepared.[1] Electron-transfer studies were carried out in the respective mixed-valent systems showing that in these molecules the ferrocenyl units are coupled electronically. However, phosphines take an exceptional position in this series, due to the fact that they are not aromatic.[2] This results in a variety of possibilities to influence the electronic communication via the phosphine motif. 2,5-Diferrocenyl-1-phenyl-1H-phosphole could be classified as moderate coupled system according to Robin and Day.[3] Herein, we report on the synthesis and (spectro-) electrochemical characterization of transition metal carbonyl complexes of 2,5-diferrocenyl-1-phenyl-1H-phosphole.

Synthesis and Characterization

The reaction behavior of 2,5-diferrocenyl-1-phenyl-1H-phosphole (1) towards metal carbonyls is presented in Scheme 1. Treatment of 1 with elemental sulfur and Fe(CO)₅ in toluene leads to the formation of 2 in which the Fe(CO)₅ building block is coordinated by the dicyan system. Complexes 3-5 were achieved by the reaction of 1 with the corresponding in situ generated [M(CO)₂(thf)] (M = Cr, Mo, W) species. Complex 2 crystallizes in the orthorhombic space group Pca2₁ (Figure 1).

Table 1. Cyclic voltammetry data.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>E°₁ in mV</th>
<th>E°₂ in mV</th>
<th>ΔE°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 [4]</td>
<td>-110 (72)</td>
<td>170 (80)</td>
<td>280</td>
</tr>
<tr>
<td>2</td>
<td>5 (75)</td>
<td>195 (81)</td>
<td>190</td>
</tr>
<tr>
<td>3</td>
<td>15 (85)</td>
<td>280 (85)</td>
<td>265</td>
</tr>
<tr>
<td>4</td>
<td>10 (77)</td>
<td>280 (61)</td>
<td>270</td>
</tr>
<tr>
<td>5</td>
<td>15 (70)</td>
<td>285 (67)</td>
<td>270</td>
</tr>
</tbody>
</table>

The ferrocenylnitrogen units of 2-5 could be oxidized separately indicating electronic interactionsthe ferrocenyldiferricenium groups. After complexation of the phosphorus atom to M(CO)₂ it was slightly decreased redox separation compared to 1 could be observed. Complex 2 shows a significant decrease of the ΔE° value after complexation of the dicyan system to Fe(CO)₅. The results of the electrochemical measurements are an indication for weakly to moderately coupled class II systems according to Robin and Day.[4]

Spectroelectrochemistry

The in situ UV-vis/NIR measurements of 2-5 were performed in an OTTLE (= Optically Transparent Thin-Layer Electrochemistry) cell. Upon oxidation a broad band between 1500 and 2500 nm appears for all compounds. A further potential increase leads to the disappearance of these absorptions, a behavior typical for involvement in charge transfer (IVCT) excitations. The observed spectra can be deconvoluted into three Gaussian-shaped bands. The sum of the Gaussian functions allows an almost exact overlay with the experimental spectra. The blue curves represent the IVCT absorptions, of which the intensity I₅₅₅, the full-width-at-half-height Δ₁₁₂ and the max values could be determined (Figure 3). As shown before, the electron transfer occurred along the dicyan system and the electronic characteristics of the phosphorus atom have just a small influence.[3]

Therefore, upon coordination of the dicyan system towards Fe(CO)₅ and the resulting lower electron density, the IVCT absorption of 2 shows a decreased intensity and increased Δ₁₁₂ value. Hence, a decrease of the interaction exists. After complexation of the phosphorus atom to M(CO)₅ (M = Cr, Mo, W) a somewhat decreased electronic communication as demonstrated by the lower intensities and the higher Δ₁₁₂ values in 3-5 was observed.

Conclusion

The transition metal complexes 2-5 have been prepared by the reaction of 2,5-diferrocenyl-1-phenyl-1H-phosphole with [M(CO)₂(thf)] (M = Cr, Mo, W) or Fe(CO)₅, respectively. Electrochemical measurements revealed a separate oxidation of the two ferrocenyl groups in 2-5, indicating an electronic communication between the ferrocenyl termini. These results were confirmed by UV-vis/NIR measurements. All four compounds exhibit IVCT absorptions of weak to moderate strength and could be classified as class II systems according to Robin and Day. A coordination of the dicyan system to Fe(CO)₅ in 2 results in a significantly lower interaction. In contrast, complexation of the phosphorus atom in 3-5 leads to a just slightly decrease of the metal-metal-interaction. This confirms the smaller impact of the phosphorus atom on the electronic communication.

References and Acknowledgement


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