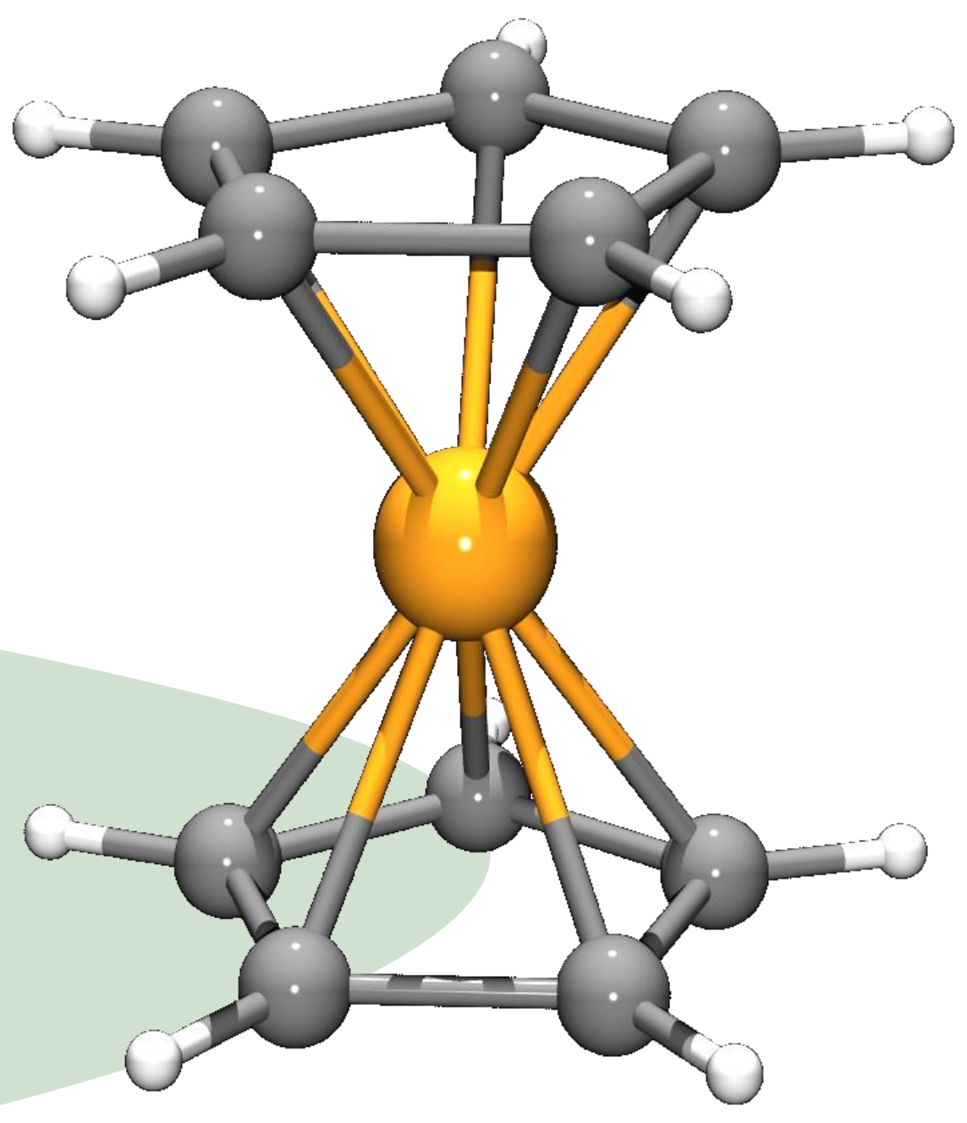
Transition Metal Complexes of 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole



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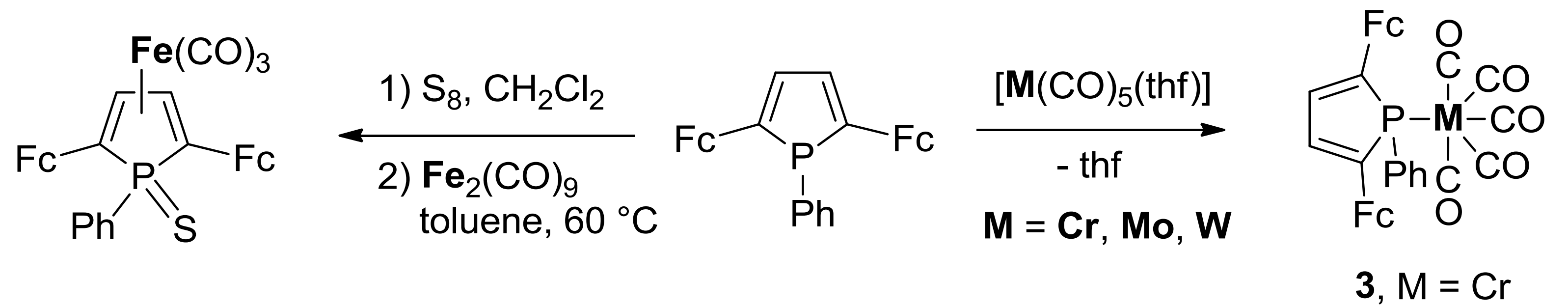
Introduction

Recently, a series of multiferrocenyl-functionalized five-membered heterocycles including furan, 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, phospholes 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 phosphole motif. 2,5-Diferrocenyl-1-phenyl-1*H*-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-1*H*-phosphole.

Synthesis and Characterization



2

1

3, M = Cr
4, M = Mo
5, M = W

Scheme 1. Synthesis of phospholes **2–5**, Fc = **Fe**(η^5-C_5H_5)(η^5-C_5H_4).

The reaction behavior of 2,5-diferrocenyl-1-phenyl-1*H*-phosphol (**1**) towards metal carbonyls is presented in Scheme 1. Treatment of **1** with elemental sulfur and **Fe**$_2$(CO)$_9$ in toluene leads to the formation of **2** in which the **Fe**(CO)$_3$ building block is coordinated by the dienic system. Complexes **3–5** were achieved by the reaction of **1** with the corresponding *in situ* generated [**M**(CO)$_5$(thf)] (M = Cr, Mo, W) species. Complex **2** crystallizes in the orthorhombic space group *Pca*2$_1$ (Figure 1).

Electrochemistry

Table 1. Cyclic voltammetry data.[a]

Compd.	$E^{\circ\prime}_1$ in mV (ΔE_p in mV)	$E^{\circ\prime}_2$ in mV (ΔE_p in mV)	$\Delta E^{\circ\prime}$ in mV
1 [3]	-110 (72)	170 (80)	280
2	5 (75)	195 (81)	190
3	15 (85)	280 (85)	265
4	10 (77)	280 (61)	270
5	15 (70)	285 (67)	270

[a] Potentials *vs* FcH/FcH$^+$, scan rate 100 mV·s^{-1} at glassy carbon electrode,1.0 mmol·L^{-1} solutions of **2–5** in dry dichloromethane; 0.1 mol·L^{-1} [N^{n}Bu$_4$][B(C_6F_5)$_4$] as supporting electrolyte at 20 °C.

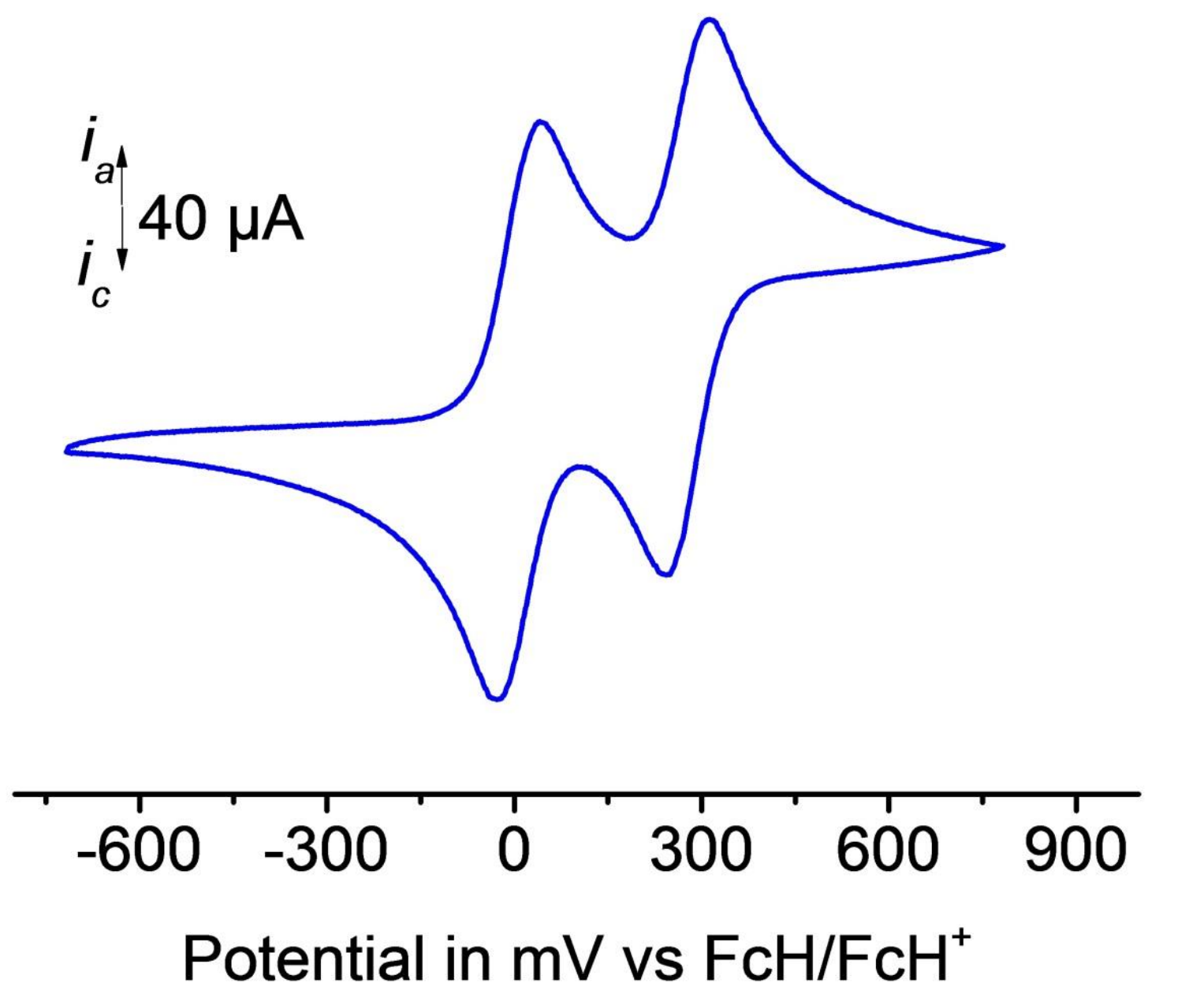


Figure 2. Cyclic voltammogram of **4**, in dichloromethane solution (1.0 mmol·L^{-1}) at 20 °C, supporting electrolyte 0.1 mol·L^{-1} [N^{n}Bu$_4$][B(C_6F_5)$_4$],
.

The ferrocenyl units of **2–5** could be oxidized separately indicating electronic interactions between the ferrocenyl/ferrocenium groups. After complexation of the phosphorus atom to **M**(CO)$_5$ a slightly decreased redox separation compared to **1** could be observed. Complex **2** shows a significant decrease of the $\Delta E^{\circ\prime}$ value after complexation of the dienic system to **Fe**(CO)$_3$. The results of the electrochemical measurements are an indication for weakly to moderatly coupled class II systems according to Robin and Day.[4]

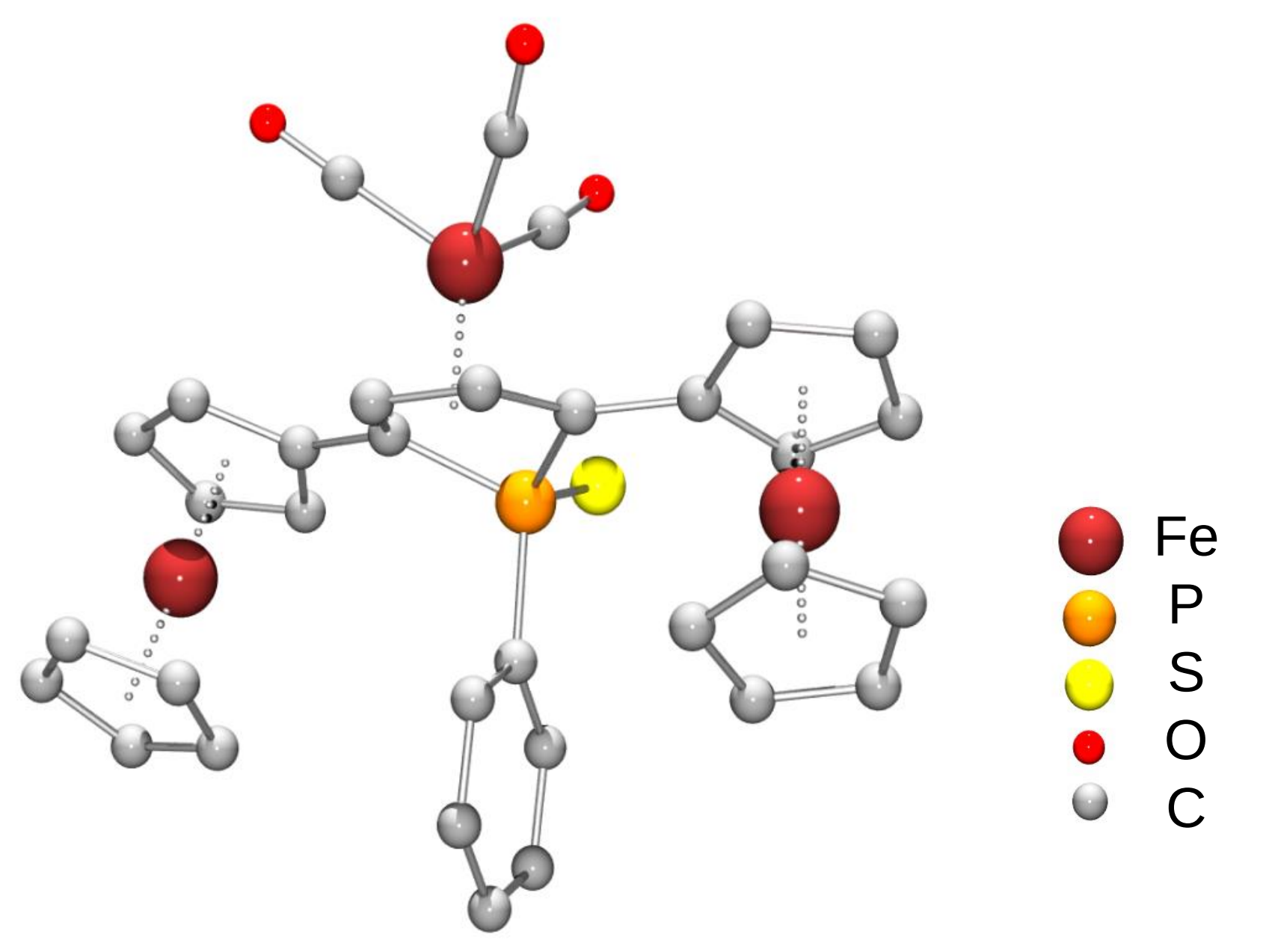


Figure 1. Molecular structure of **2** in the solid state.

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 intervalence 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 ε_{max}, the full-width-at-half-height $\Delta\nu_{1/2}$ and the ν_{max} values could be determined (Figure 3). As shown before, the electron transfer occurred along the dienic system and the electronic characteristics of the phosphorus atom have just a small influence.[3]

Therefore, upon coordination of the dienic system towards **Fe**(CO)$_3$ and the resulting lower electron density, the IVCT absorption of **2** shows a decreased intensity and increased $\Delta\nu_{1/2}$ 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 $\Delta\nu_{1/2}$ values in **3–5** was observed.

Table 2. NIR data of phospholes [**2**]$^+$–[**5**]$^+$ and [**1**]$^+$ for comparison..

Compd.	ν_{max} (cm^{-1}) (ε_{max} (L·mol^{-1}·cm^{-1}))	$\Delta\nu_{1/2}$ (cm^{-1})
[**1**]$^+$ [3]	5000 (1750)	3050
[**2**]$^+$	5050 (400)	4700
[**3**]$^+$	4850 (1450)	3300
[**4**]$^+$	4850 (1650)	3200
[**5**]$^+$	4850 (1450)	3250

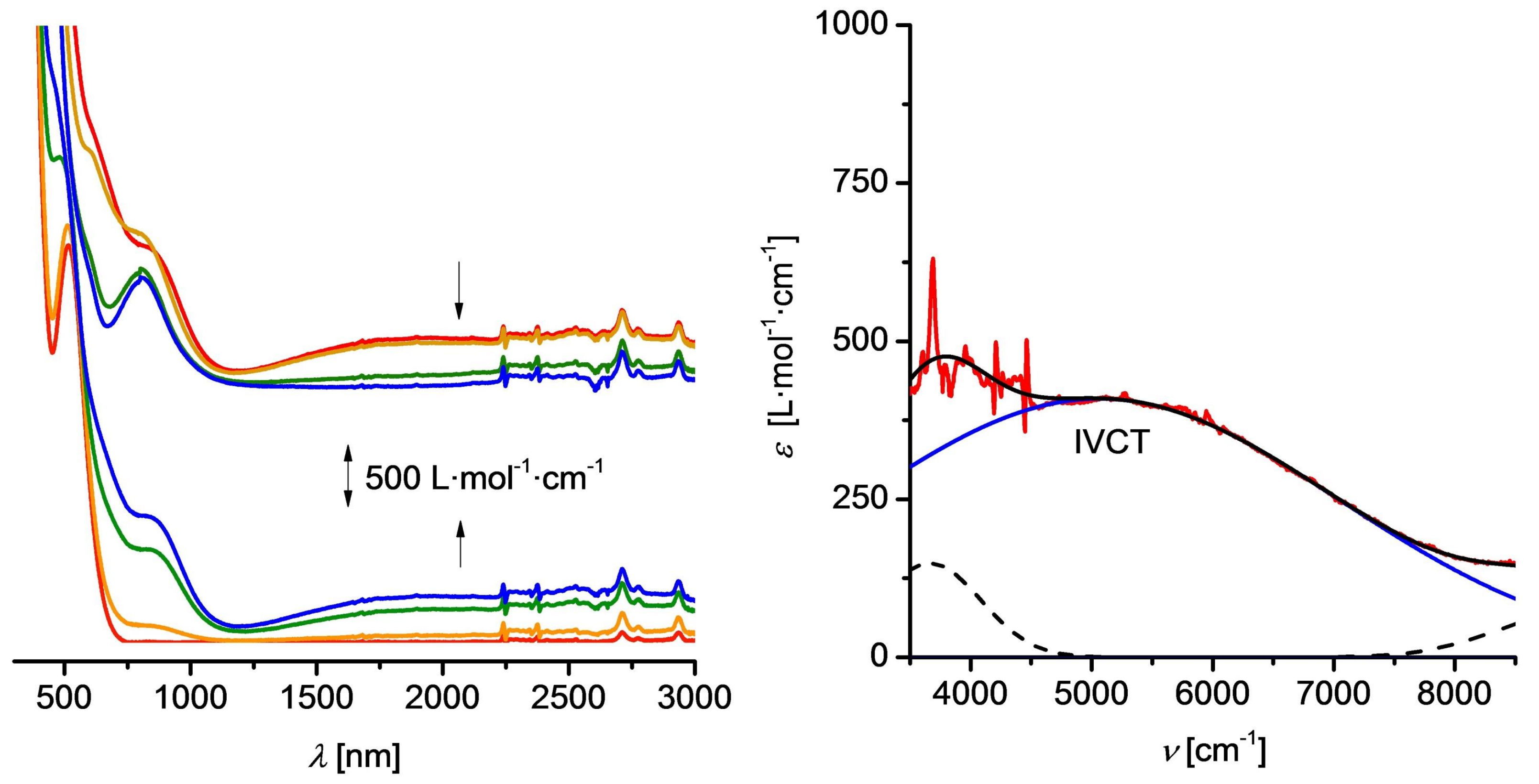


Figure 3. Left: UV-vis/NIR spectra of **2** at rising potentials (bottom: -200 to 500 mV; top: 500 to 1000 mV vs Ag/AgCl). Right: Deconvolution of the NIR absorptions of [**2**]$^+$.

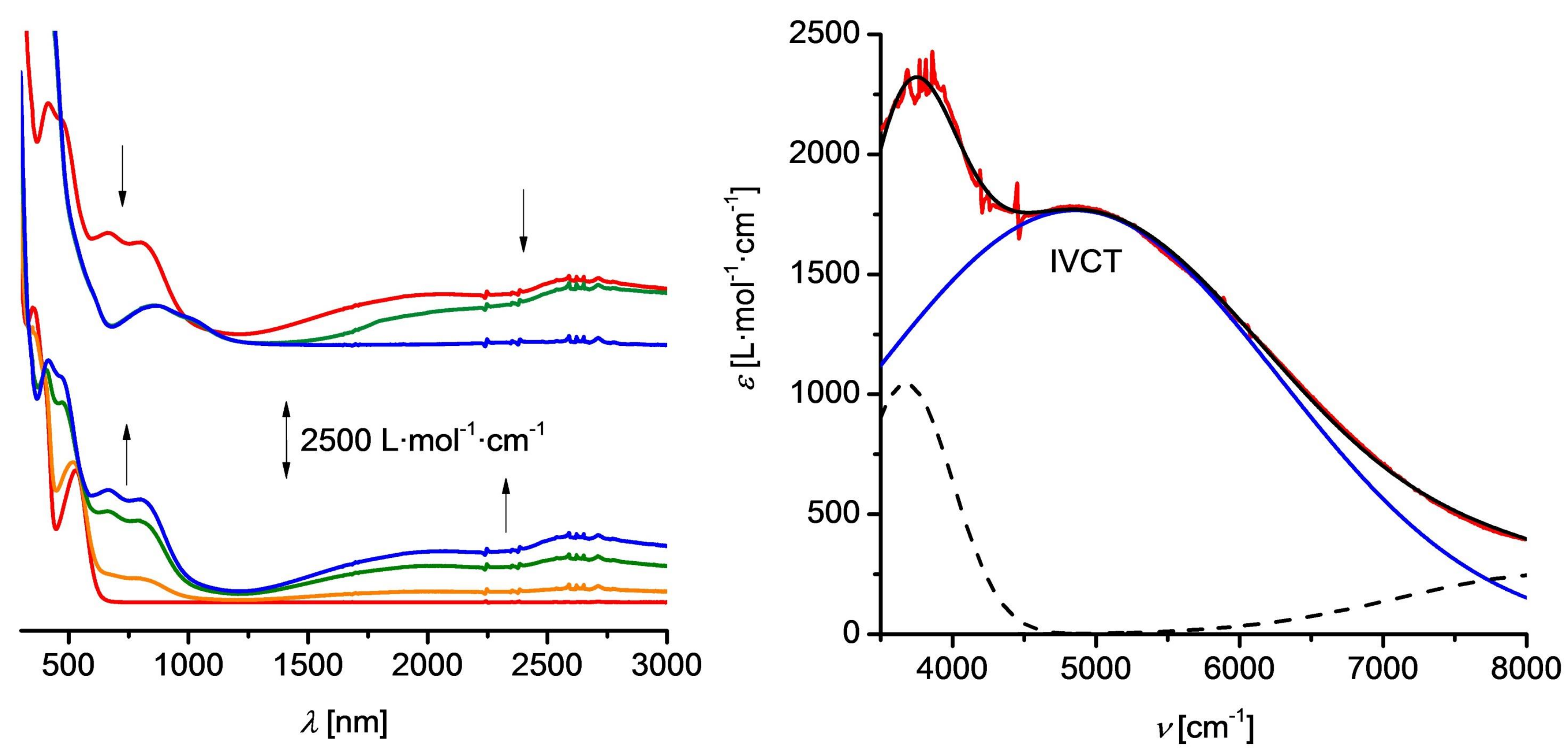


Figure 4. Left: UV-vis/NIR spectra of **4** at rising potentials (bottom: -200 to 450 mV; top: 450 to 1000 mV vs Ag/AgCl). Right: Deconvolution of the NIR absorptions of [**4**]$^+$.

Conclusion

The transition metal complexes **2–5** have successfully been prepared by the reaction of 2,5-diferrocenyl-1-phenyl-1*H*-phosphol with [**M**(CO)$_5$(thf)] (M = Cr, Mo, W) or **Fe**$_2$(CO)$_9$, 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 dienic system to **Fe**(CO)$_3$ in **2** results in a signifiquantly 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

[1] For example: (a) A. Hildebrandt, H. Lang, *Dalton Trans*. **2011**, *40*, 11831-11837. (b) A. Hildebrandt, D. Schaarschmidt, R. Claus, H. Lang, *Inorg. Chem*. **2011**, *50*, 10623-10632. (c) A. Hildebrandt, H. Lang, *Organometallics* **2013**, *32*, 5640-5653.
[2] L. Nyulászi, *Chem. Rev*. **2001**, *101*, 1229-1246.
[3] D. Miesel, A. Hildebrandt, M. Korb, P. J. Low, H. Lang, *Organometallics* **2013**, *32*, 2993-3002.
[4] R. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

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