

# 1',1'''-Bis(ethynyl)biferrocene as a Linking Group for Ruthenium and Osmium Halfsandwich Fragments: Synthesis, Solid State Structure and Spectro-Electrochemistry



M. Lohan, F. Justaud, a) C. Lapinte, a) and H. Lang\*

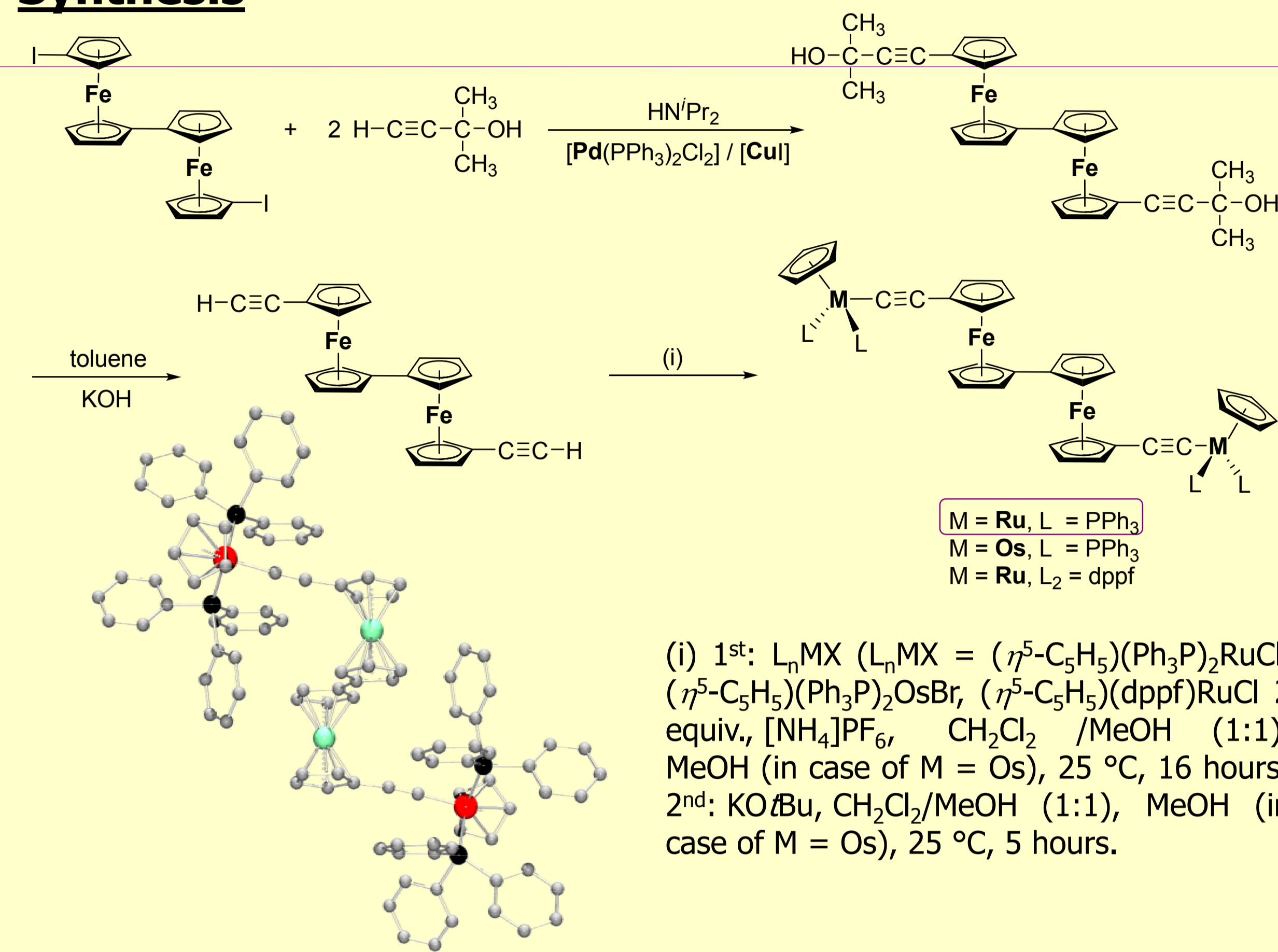


Institut für Chemie, Lehrstuhl für Anorganische Chemie, Fakultät für Naturwissenschaften, Technische Universität Chemnitz, Straße der Nationen 62, 09111 Chemnitz. E-mail: heinrich.lang@chemie.tu-chemnitz.de a) UMR CNRS 6226 Sciences Chimiques de Rennes, Université de Rennes 1, Campus de Beaulieu, F-35042 Rennes.

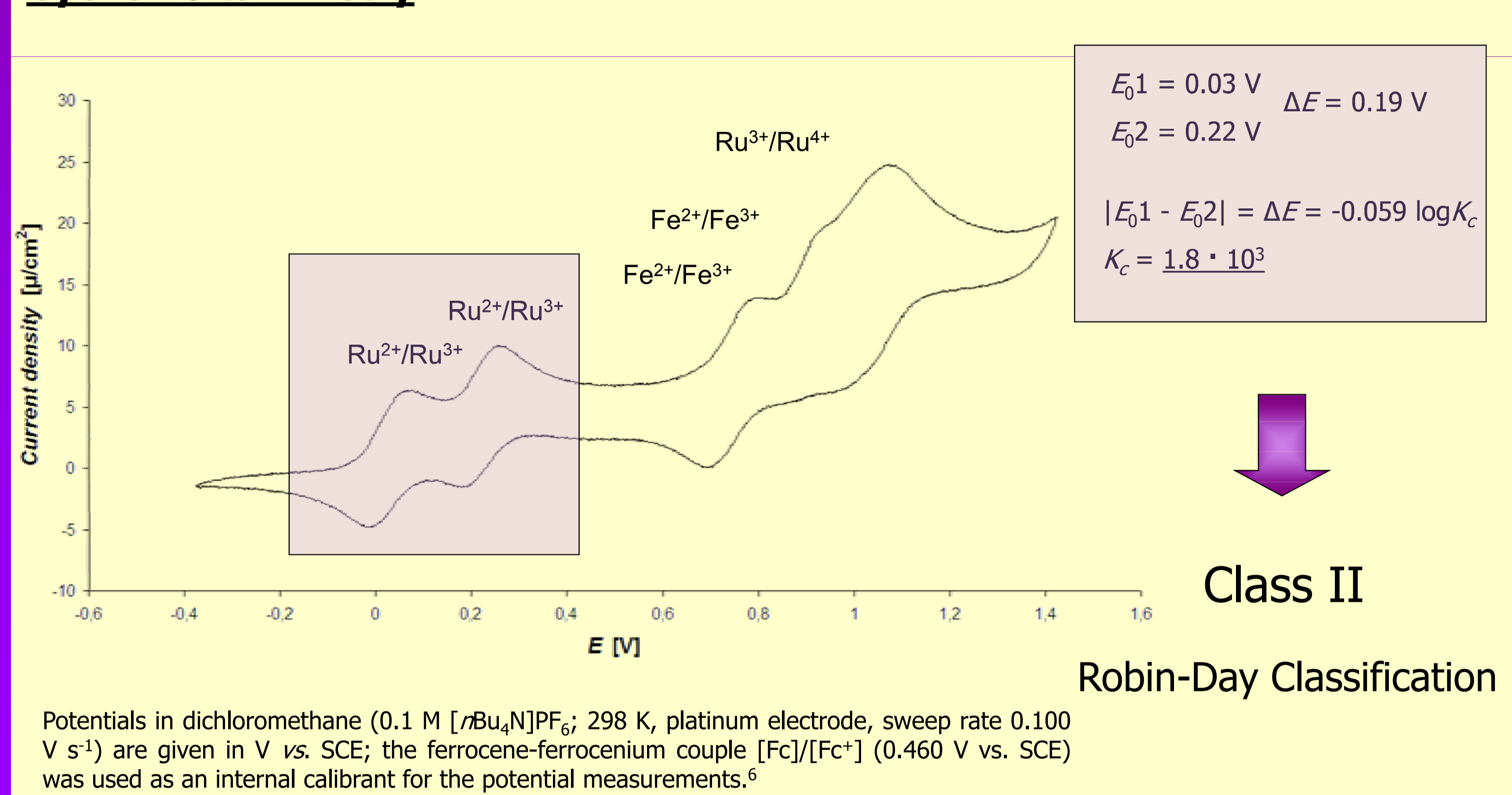
## Introduction

Complexes in which two redox-active transition metal atoms are connected *via* carbon-rich ( $\pi$ -conjugated) organic bridging units have received increasing attention during the last years.<sup>1</sup> The use of an organometallic biferrocene spacer has attracted much attention because it easily forms mixed-valent Fe(II)-Fe(III) species by electrochemical or chemical oxidation.<sup>2</sup> Molecules of type  $(L_nMC\equiv C)_2bfc$  ( $L_nM = (\eta^5-C_5H_5)(Ph_3P)_2Ru$ ,  $(\eta^5-C_5H_5)(Ph_3P)_2Os$ ,  $(\eta^5-C_5H_5)(dppf)Ru$ ;  $bfc = 1',1'''$ -biferrocenyl,  $((\eta^5-C_5H_4)_2Fe)_2$ ;  $dppf = 1,1'$ -bis(diphenyl)phosphanylferrocene,  $(\eta^5-C_5H_4PPh_2)_2Fe$ ) are of interest, due to their robustness, electron richness and their rigid geometry. Because of their conjugation, they can form multiple electroactive systems. Bis(ethynyl)biferrocenes can be considered as bridging and redox-active units between transition metal fragments allowing communication through delocalized bonds in the respective array.<sup>1,3,4</sup> We here report a straightforward synthesis methodology to prepare ruthenium- and osmium-containing bis(ethynyl)biferrocenes. Electrochemical studies together with electron paramagnetic resonance measurements of corresponding radical cations in-situ prepared by chemical oxidation and UV-vis and NIR spectroscopic studies are also reported.

## Synthesis

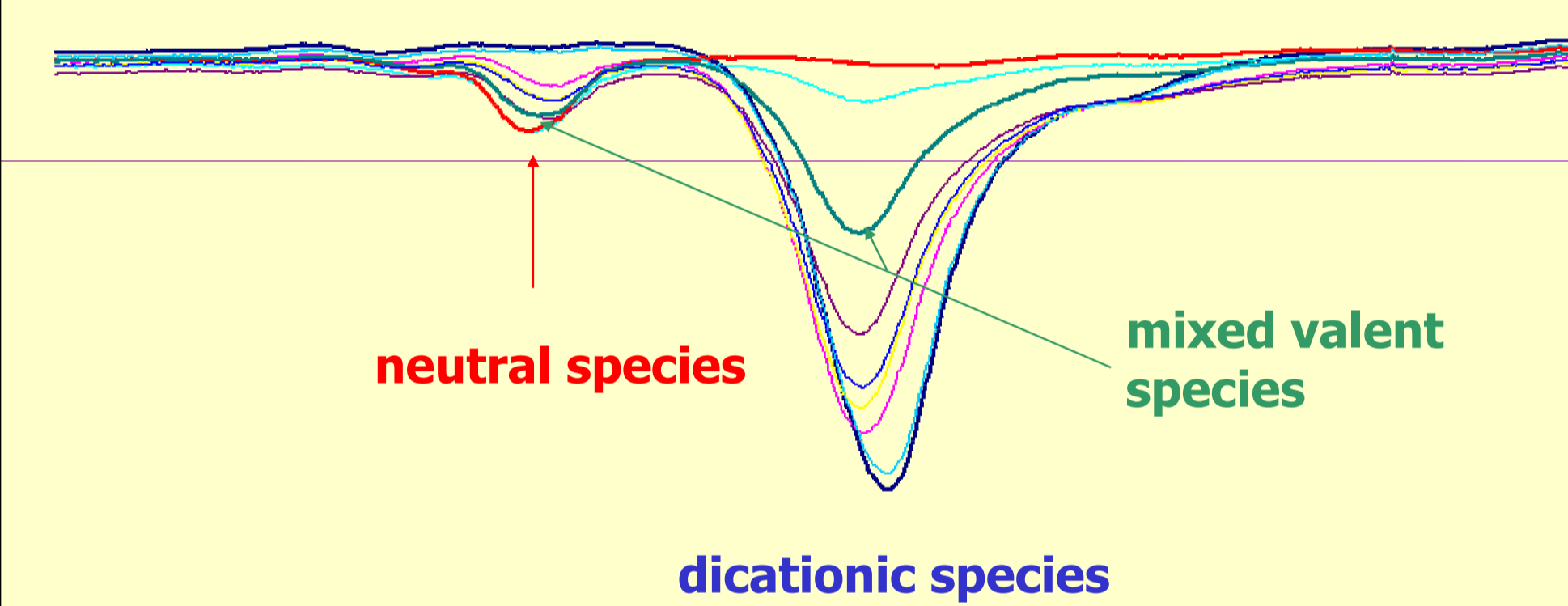


## Cyclic Voltammetry

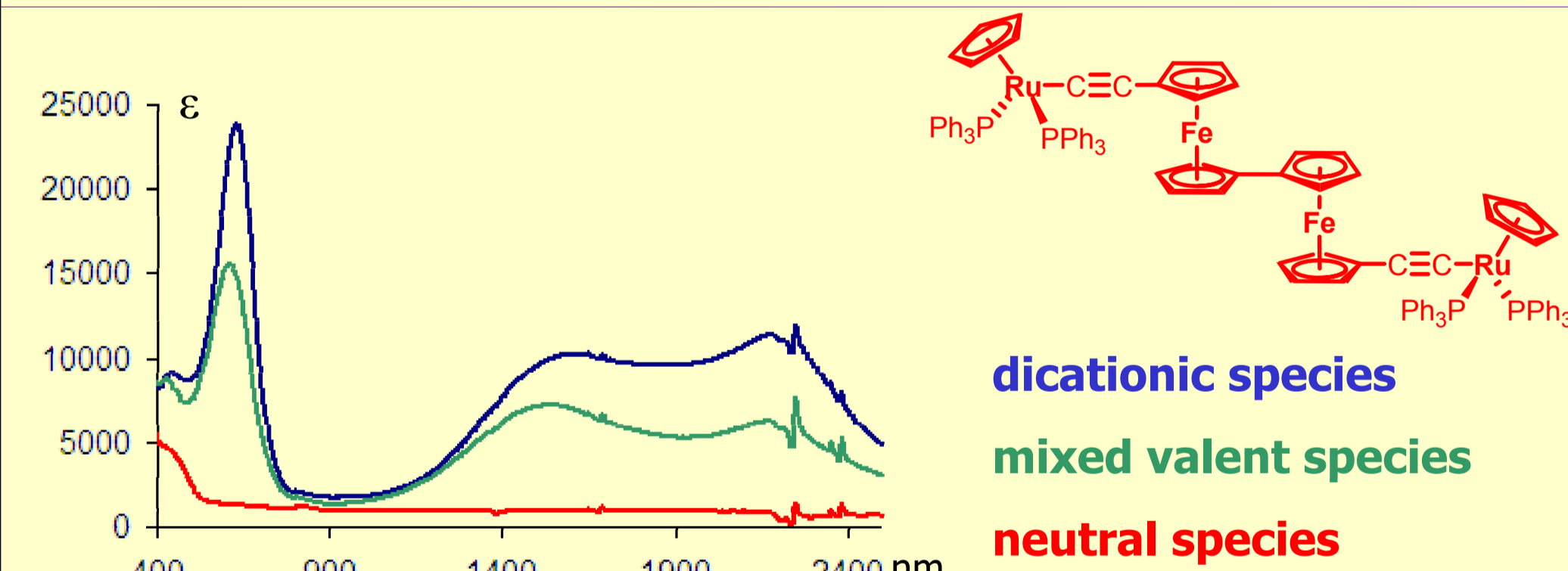


## Spectroelectrochemistry

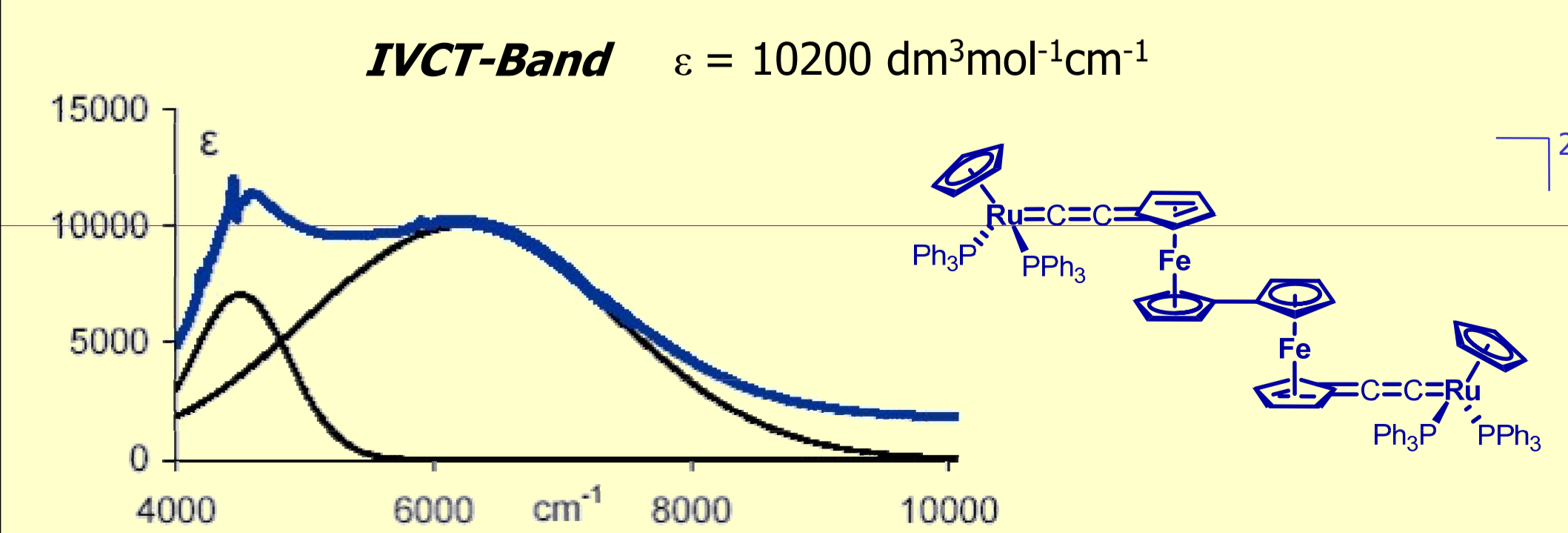
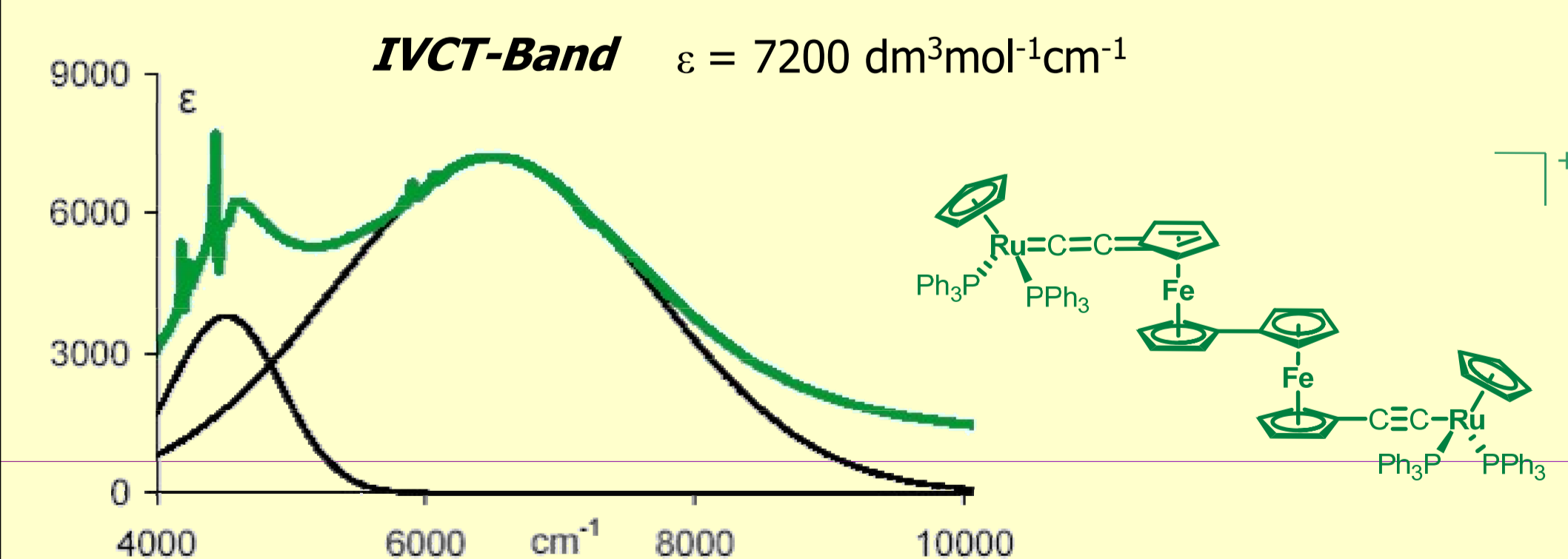
### IR-Spectroscopy (in-situ Oxidation)



### UV-Vis/NIR-Spectroscopy (in-situ Oxidation)



### NIR-Spectroscopy of Chemical Oxidized Species



## UV-Vis Spectroscopy

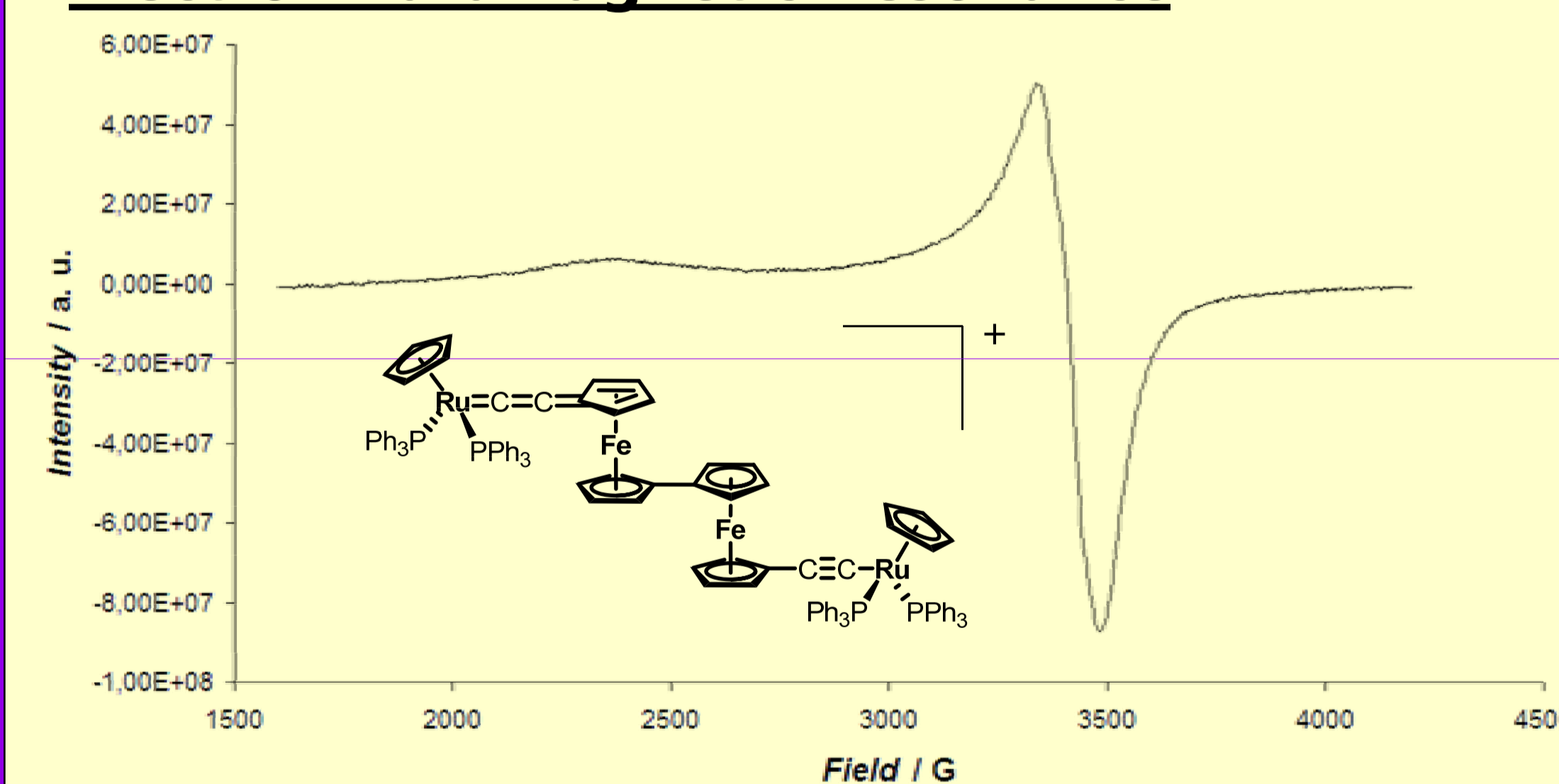
Compd. a)	Absorption $\lambda/nm$ ( $10^{-3} \epsilon/dm^3 mol^{-1} cm^{-1}$ )
<b>bfc(C≡CH)<sub>2</sub></b>	227 (75), 265 (24), 301 (13), 450 (0,8)
<b>bfc(C≡C(CpRu(PPh<sub>3</sub>)<sub>2</sub>))<sub>2</sub></b>	227 (135), 345 (22), 440 (5)
<b>bfc(C≡C(CpOs(PPh<sub>3</sub>)<sub>2</sub>))<sub>2</sub></b>	227 (161), 272 (46), 350 (22), 440 (4)
<b>bfc(C≡C(CpRudppf))<sub>2</sub></b>	270 (147), 347 (10), 438 (2)

a) Measured at 25 °C in  $CH_2Cl_2$ , Cp =  $\eta^5-C_5H_4$ .

Compd. a)	$[Ru^{2+}]/[Ru^{3+}]$ $E(\Delta E_p, I_p/I_a)$ [V]	$[Fe^{2+}]/[Fe^{3+}]$ $E(\Delta E_p, I_p/I_a)$ [V]	$K_c$
<b>bfc(C≡CH)<sub>2</sub></b>		0.47 (0.13, ~1) 0.85 (0.13, ~1)	
<b>bfc(C≡C(CpRu(PPh<sub>3</sub>)<sub>2</sub>))<sub>2</sub></b>	0.03 (0.09, 1) 0.22 (0.10, 1)	0.74 (0.12, <1) 0.89 <sup>b)</sup>	1.8 · 10 <sup>3</sup>

a) Redox potentials determined as  $(E_p + E_a)/2$  for the reversible or partially reversible couples and as  $E_p$  for the not reversible redox systems.  
b) Irreversible. Cp =  $\eta^5-C_5H_4$ .

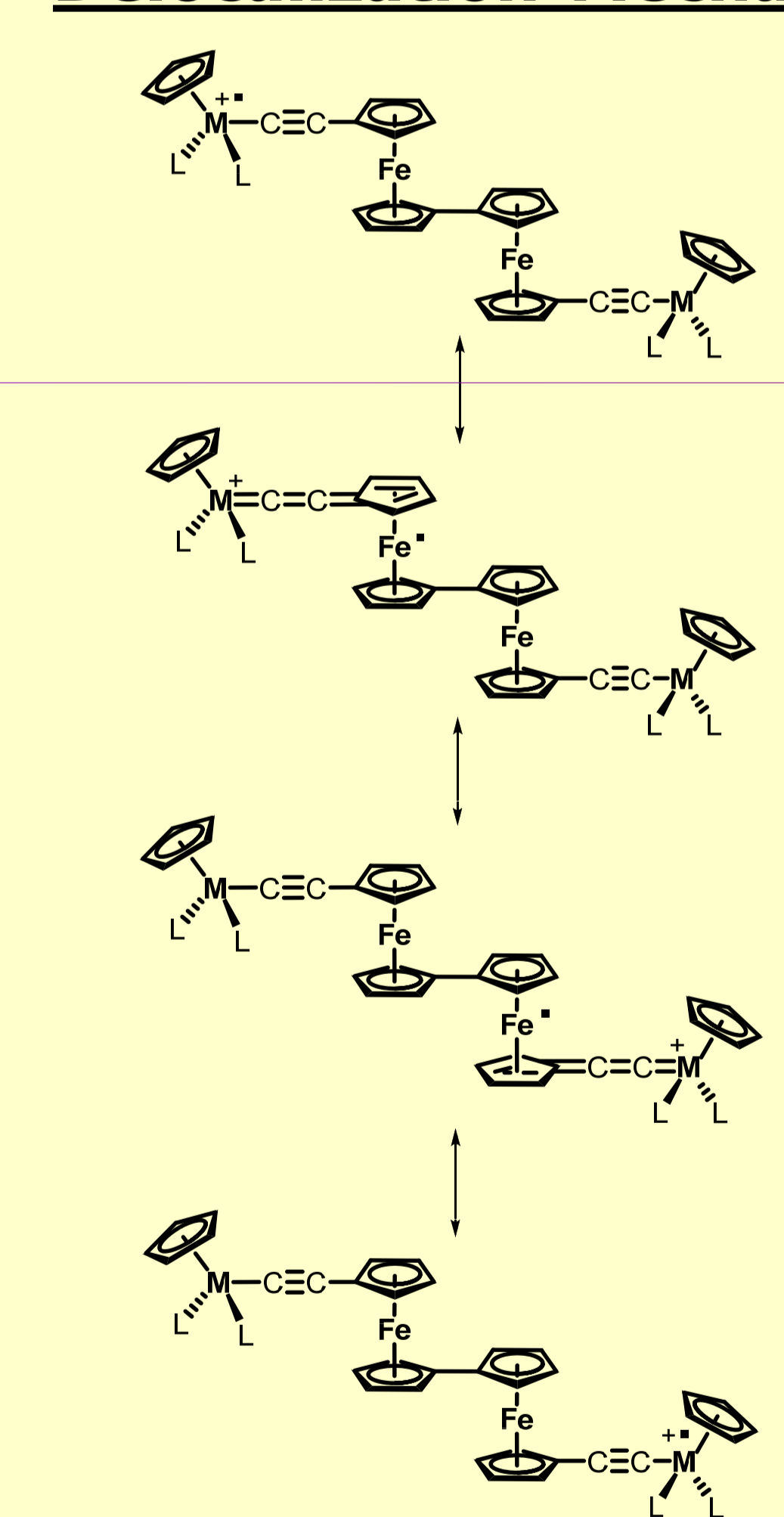
## Electron Paramagnetic Resonance



Compd. a)	$g_{  }$	$g_{\perp}$	$\Delta g^b)$
<b>[bfc(C≡CH)<sub>2</sub>]<sup>+</sup></b>	3.24	1.91	1.33
<b>[bfc(C≡CH)<sub>2</sub>]<sup>2+</sup>c)</b>	3.46	1.86	1.60
<b>[bfc(C≡C(CpRu(PPh<sub>3</sub>)<sub>2</sub>))<sub>2</sub>]<sup>+</sup></b>	2.852	1.984	0.868
<b>[bfc(C≡C(CpRu(PPh<sub>3</sub>)<sub>2</sub>))<sub>2</sub>]<sup>2+</sup></b>	2.885	1.986	0.899
<b>[bfc(C≡C(CpOs(PPh<sub>3</sub>)<sub>2</sub>))<sub>2</sub>]<sup>+</sup></b>	2.840	2.066	0.774
<b>[bfc(C≡C(CpRudppf))<sub>2</sub>]<sup>+</sup></b>	2.828	2.009	0.819

a) Measured at 66 K. b)  $\Delta g = g_{||} - g_{\perp}$ . c) Generated using [AgOTf]. Cp =  $\eta^5-C_5H_4$ .

## Delocalization-Mechanism



## Conclusion

A series of bis(ethynyl)biferrocene-based transition metal complexes of structural type  $(L_nMC\equiv C)_2bfc$  ( $L_nM = (\eta^5-C_5H_5)(Ph_3P)_2Ru$ ,  $(\eta^5-C_5H_5)(Ph_3P)_2Os$ ,  $(\eta^5-C_5H_5)(dppf)Ru$ ),  $bfc = 1',1'''$ -biferrocenyl,  $((\eta^5-C_5H_4)_2Fe)_2$ ;  $dppf = 1,1'$ -bis(diphenyl)phosphanylferrocene  $(\eta^5-C_5H_4PPh_2)_2Fe$ ) have been synthesized. The cyclic voltammetric data of these compounds indicate that the 1',1'''-bis(ethynyl)biferrocene unit acts as a linking group for ruthenium and osmium halfsandwich fragments capable to convey electronic interaction from one end to the other more efficiently than 1,1'-(ethynyl)ferrocene, which was recognized to behave as an insulator for a model with the same terminal ends.<sup>5</sup> EPR spectroscopy allowed to establish that the SOMOs, which contain the odd electrons in the respective mixed valent species, possess a significant biferrocene character. Interestingly, the small tensors of anisotropy strongly support that the biferrocenyl bridge acts as a relay in this long distance electron transfer process. Analysis of the NIR absorption bands also supports that a direct Ru-Ru electron transfer does not take place in  $[bfc(C\equiv C(\eta^5-C_5H_5Ru(PPh_3)_2))_2]^{2+}$ , the electron exchange occurring through two successive  $Ru\equiv C\equiv C\equiv Fe$  electron-transfers favored by a fast exchange between the two ferrocenyl units. The experimental data support that the strongest interaction may occur between one  $(\eta^5-C_5H_5)(PPh_3)_2M$  moiety and the biferrocenyl unit through ethynyl fragments, but while the ferrocene group acts as an insulator, the biferrocene connectivity plays the role of a relay allowing electron-transfer from one metal terminus to the other one.

## References

- [1] For example: (a) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 2586. (b) Ceccan, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004**, *248*, 683. [2] (a) Brown, G. M.; Meyer, T. J.; Cowan, D. O.; Le Vanda, C.; Kaufmann, F. J.; Roling, P. V.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 506. (b) Mueller-Westerhoff, U. T.; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702. [3] For example: (a) Long, N. J.; Martin, A. J.; Vilar, R.; White, A. J. P.; Williams, D. J.; Younus, M. *Organometallics* **1999**, *18*, 4261. (b) Colbert, M. C. B.; Hodgson, D.; Lewis, J.; Raithby, P. R.; Long, N. J. *Polyhedron* **1995**, *14*, 2759. (c) Dong, T.-Y.; Lin, H.-Y.; Lin, S.-F.; Huang, C.-C.; Wen, Y.-S.; Lee, L. *Organometallics* **2008**, *27*, 555. [4] (a) Köcher, S.; van Klink, G. P. M.; van Koten, G.; Lang, H. *Journal of Organometallic Chemistry* **2006**, *691*, 3319. (b) Lohan, M.; Ecorchard, P.; Rüffer, T.; Justaud, F.; Lapinte, C.; Lang, H. *Organometallics* **2009**, *28*, 1878. [5] (a) Bruce, M. I.; Low, P. J.; Hartl, F.; Humphrey, P. A.; de Montigny, F.; Jevric, M.; Lapinte, C.; Perkins, G. J.; Roberts, R. L.; Skelton, B. W.; White, A. H. *Organometallics* **2005**, *24*, 5241. (b) Sato, M.; Shintate, H.; Kawata, Y.; Sekino, M.; Katada, M.; Kawata, S. *Organometallics* **1994**, *13*, 1956. [6] (a) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461. (b) Strehlow, H.; Knoche, W.; Schneider, H. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 760.