Organometallic Chemistry With Emphasis On Electron Transfer Studies

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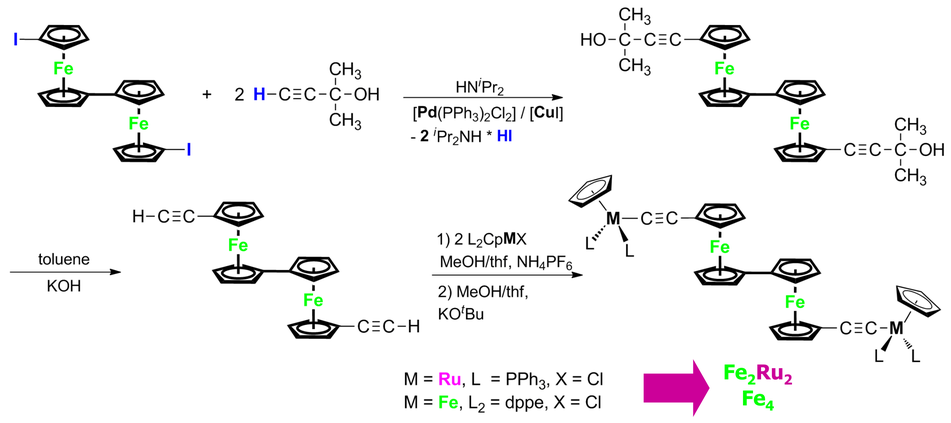
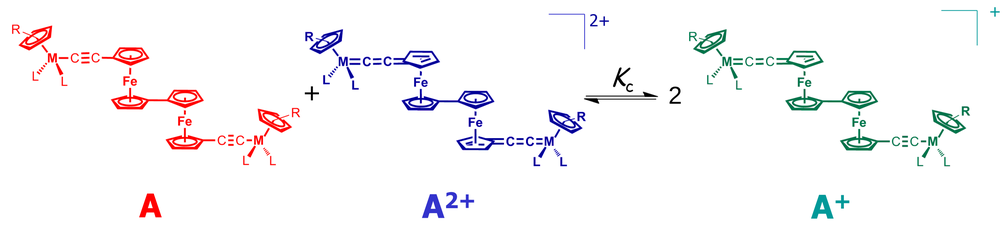
Introduction

The linkage of transition-metal fragments to give (hetero)multimetallic molecules is, from the viewpoint of synthetic chemistry, a challenge, since the molecular design of such assemblies requires the accessibility of multitopic bridging units featuring diverse reactive coordination sites. [1] In the frame of our previous work in this field of chemistry, the consecutive synthesis, characterization, and structure of heterotri- to heteroheptametallic transition metal complexes in a straightforward way was discussed. [1,2] For understanding the interaction of multiple metal centers via an organic bridge, it is necessary to study smaller symmetric molecules, *e. g.* M–(C≡C)$_n$–M. [3] The use of an organometallic spacer, for example, biferrocenyl between two redoxactive termini, has attracted much attention because mixed-valent Fe(II)-Fe(III) species are easily formed by electrochemical or chemical oxidation. [4] Bis(ethynyl)biferrocene can be considered as a bridging and redox-active connectivity between transition metal fragments allowing communication through delocalized bonds in the respective array. [5,6] The Synthesis, characterization and bonding of selected (hetero)- and (homo)metallic complexes will be presented. The spectroelectrochemistry of these molecules will be described including UV-Vis-NIR-, IR-, EPR-, Mößbauer-spectroscopy, and cyclovoltammetry.

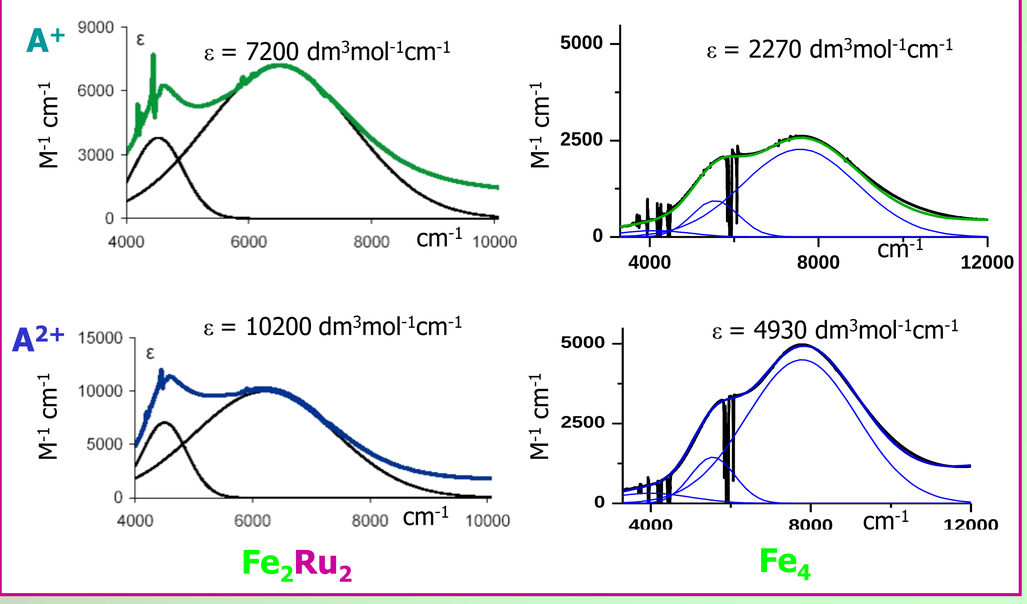
Synthesis



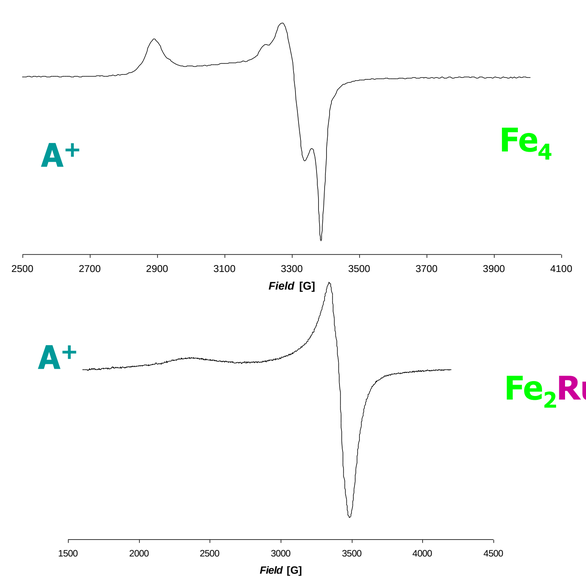
Comproportionation Equilibrium



NIR Spectroscopy of Chemical Oxidized Species



Electron Paramagnetic Resonance



- Unpaired electrons centered at Fe(η^2-dppe)(Cp*)
- Communication between Fe- and biferrocene moiety is slower than EPR time-scale

Weak communication between the terminal Fe centers

- Unpaired electrons not Ru-centered
- SOMOs show biferrocenium character (bfc$^+$)
- Electron delocalization between the two ferrocene moieties

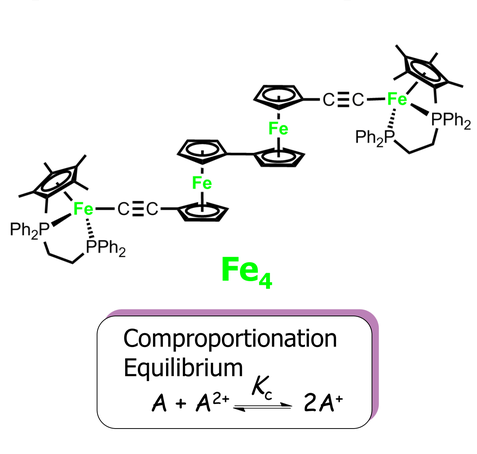
Communication between Ru and Fe

Mössbauer spectroscopy [a)]

Compd. [a)]	Fe(η^2-dppe)(Cp*)		bfc		Relative surface areas
	IS	Qs	IS	QS	
Fe$_4$	0.26	1.95	0.54	2.32	1:1
Fe$_4$[PF$_6$]	0.27 0.23	1.98 0.95	0.52	2.24	25:26:49
Fe$_4$[PF$_6$]$_2$	0.22	0.99	0.51	2.18	1:1
Fe$_4$[PF$_6$]$_3$	0.21	1.02	0.5 0.5	2.11 0.42	61:19:20

a) The velocity is referenced to the iron metal, data in mm/s; Fe$_4$ = bfc(C≡C(Fe(η^2-dppe)Cp*))$_2$.

Cyclic Voltammetry



ΔE = 0.08 V

ΔE = 0.059 logK_c

K_c = 24

ΔE = 0.19 V

ΔE = 0.059 logK_c

K_c = 1.7 · 10^3

Compd.	[M^{2+}]/[M^{3+}] E(ΔE_p, I_c/I_a) [V]	[Fe^{2+}]/[Fe^{3+}] E(ΔE_p, I_c/I_a) [V]	*Kc*
bfc(C≡CH)$_2$		0.47 (0.13, ~1) 0.85 (0.13, ~1)	
bfc(C≡C(CpRu(PPh$_3$)$_2$))$_2$	0.03 (0.09, 1) 0.22 (0.10, 1)	0.74 (0.12, <1) 0.89[a)]	1.8·10^3
bfc(C≡C(Cp*Fe(dppe)))$_2$	-0.23 (0.11)	0.49 (0.07) 0.78 (0.07)	24

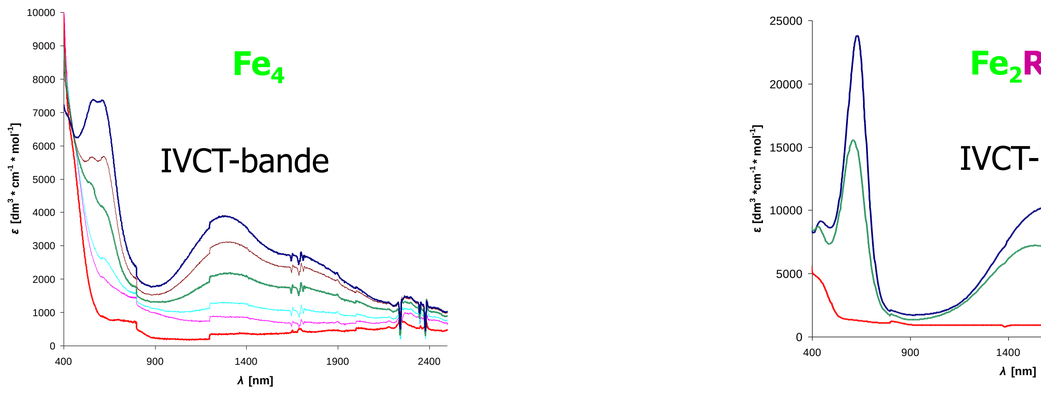
Potentials in dichloromethane (0.1 M [^{n}Bu$_4$N]PF$_6$; 298 K, platinum electrode, sweep rate 0.100 V s^{-1}) are given in V *vs.* SCE; the ferrocene-ferrocinium couple [Fc]/[Fc$^+$] (0.460 V *vs.* SCE) was used as an internal calibrant for the potential measurements. [7] a) Irreversible. Cp = η^5-C$_5$H$_5$; Cp* = η^5-C$_5$Me$_5$; bfc = 1′,1‴-biferrocenyl; ((η^5-C$_5$H$_4$)$_2$Fe)$_2$; dppe = 1,2-bis(diphenylphosphino)ethane.

Class II

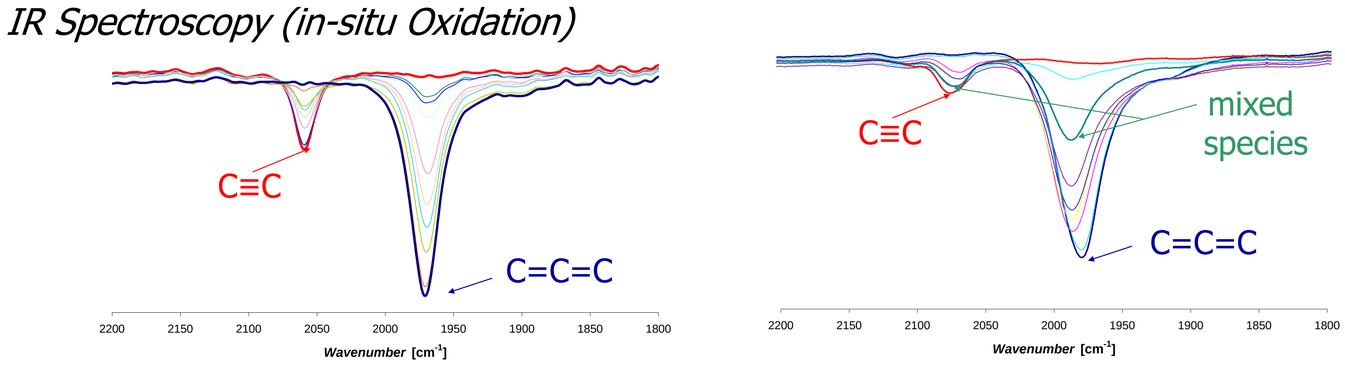
Robin and Day

Spectroelectrochemistry

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



IR Spectroscopy (in-situ Oxidation)



Conclusion

A series of bis(ethynyl)biferrocenyl-based transition metal complexes of structural type (L$_n$MC≡C)$_2$bfc (L$_n$M = (η^5-C$_5$H$_5$)(Ph$_3$P)$_2$Ru, (η^5-C$_5$Me$_5$)(dppe)Fe, bfc = 1′,1‴- biferrocenyl, ((η^5-C$_5$H$_4$)$_2$Fe)$_2$; dppe = 1,1′-bis(diphenyl)phosphanylethane) have been synthesized. The cyclic voltammetry data of these compounds indicate that the 1′,1‴-bis(ethynyl)biferrocenyl unit acts as a linking group for ruthenium and iron halfsandwich fragments capable of conveying electronic interaction from one end to the other more efficiently than 1,1′-(ethynyl)ferrocene (with the same terminal groups), which was recognized to behave as an insulator [5]. EPR spectroscopy allowed to establish in case of Fe$_2$Ru$_2$ 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. In case of Fe$_4$ one can see from EPR that the unpaired electron is centered at the half-sandwich Iron-ion. The electron transfer process between the iron half-sandwich moiety and the biferrocenyl-bridge is slower than EPR timescale. Analysis of the NIR absorption bands also supports that a direct M-M electron transfer does not take place in [bfc(C≡C(Cp′)M(L)$_2$)$_2$]$^{2+}$ (M = Fe, Cp′ = Cp*, L$_2$ = dppe; M = Ru, Cp′ = Cp, L$_2$ = 2 PPh3), the electron exchange occurs through two successive MC≡CFc electron-transfers, favored by a fast exchange between the two ferrocenyl units. The experimental data support that the strongest interaction may occur between one (Cp′)(L)$_2$M moiety and the biferrocenyl unit through ethynyl fragments but while the ferrocenyl group acts as an insulator, the biferrocene connectivity plays the role of a relay allowing electron-transfer from one metal terminus to the other.

References

[1] R. Packheiser, P. Ecorchard, T. Rüffer and H. Lang, *Chem. Eur. J.*, 2008, **14**, 4948 and references therein. [2] H. Lang, K. Köhler and S. Blau, Coord. *Chem. Rev.*, 1995, **143**, 113 and references therein. [3] For example: H. Jiao, K. Costuas, J. A. Gladysz, J.-F. Halet, M. Guillemot, L. Toupet, F. Paul and C. Lapinte, *J. Am. Chem. Soc.,* 2003, **125**, 9511. [4] (a) G. M. Brown, T. J. Meyer, D. O. Cowan, C. Le Vanda, F. J. Kaufmann, P. V. Roling and M. D. Rausch, *Inorg. Chem.*, 1975, **14**, 506. (b) U. T. Mueller-Westerhoff, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 702. [5] For example: (a) N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams, and M. Younus, *Organometallics*, 1999, **18**, 4261. (b) T.-Y. Dong, H.-Y. Lin, S.-F. Lin, C.-C. Huang, Y.-S. Wen, and L. Lee, *Organometallics*, 2008, **27**, 555. (c) Hore, L.-A.; McAdam, C. J.; Kerr, J. L.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *Organometallics* **2000**, *19*, 5039. Köcher, S.; van Klink, G. P. M.; van Koten, G.; Lang, H. *Journal of Organometallic Chemistry* **2006**, *691*, 3319. [6] (a) M. Lohan, P. Ecorchard, T. Rüffer, F. Justaud, C. Lapinte and H. Lang, *Organometallics*, 2009, **28**, 1878. (b) M. Lohan, F. Justaud, T. Roisnel, P. Ecorchard, T. Rüffer, H. Lang and C. Lapinte, *Organometallics*, 2009, *in press*. [7] Connelly, N. G.; Geiger, W. E., *Chem. Rev.* **1996**, *96*, 877-910.