



Introduction

Recently, we investigated a number of ferrocenyl-substituted 5-membered heterocycles regarding the electronic interaction between the Fc/Fc⁺ units via the heterocyclic core in the appropriate mixed-valent species.^[1] Thereby, phospholes offer interesting possibilities to influence the metal-metal interaction of terminal Fc units, due to the

pyramidal geometry of the phosphorus and the resulting reactive lone-pair of electrons and dienic system.^[2] A possibility to increase the delocalization within the phosphole ring is the use of sterically demanding substituents bonded to the phosphorus atom as shown by Quin and Keglevich.^[3]

Variable-Temperature NMR

An increase of the steric demand of the substituents results in decreased activation enthalpies ΔH^\ddagger . Compound **5** with the bulky *tert*-butyl groups exhibits the lowest inversion barrier within this series as demonstrated by a coalescence temperature below -100°C .

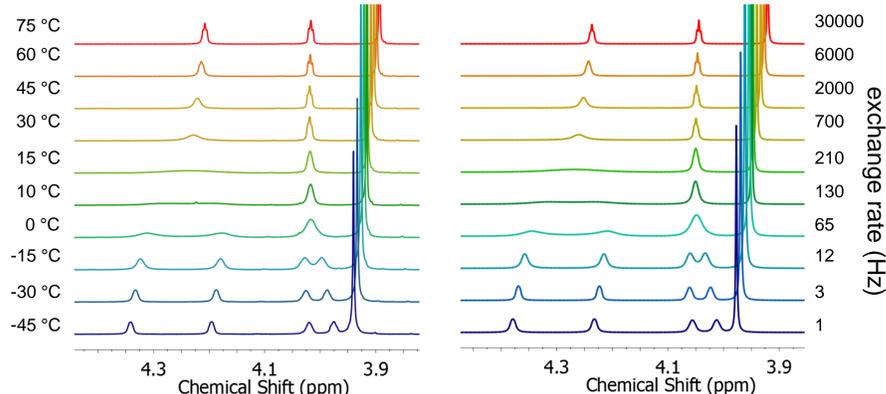


Figure 1. Experimental (left) and simulated (right) ¹H NMR spectra of the ferrocenyl protons for **4** (in toluene-*d*₆).

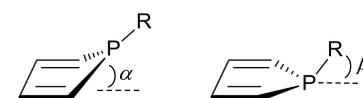
Table 1. Activation enthalpies ΔH^\ddagger and activation entropies ΔS^\ddagger .

Compd	ΔH^\ddagger (kJ·mol ⁻¹)	ΔS^\ddagger (J·mol ⁻¹ ·K ⁻¹)	Coalescence temperature (°C)
1	57.9 (±3.3)	-37.8 (±10.1)	60–75
2	61.3 (±2.9)	3.1 (±11.3)	-15–0
3	50.0 (±3.6)	-20.3 (±12.8)	-10–30
4	54.0 (±2.2)	-12.8 (±7.7)	0–15
5	-	-	<-100

X-ray Discussion

Table 2. Geometric data for **2–5**.

Geometric Features	2	3	4	5
α	6	15	11	16
β	67	59	61	44
sum of angles around P	302	312	310	331
Bird Index	20	32	30	46



The geometric criteria are an indication for an increase of planarity of the pyramidal phosphorus environment in **5** and hence an increase of delocalization in the heterocyclic ring.

(Spectro)Electrochemistry

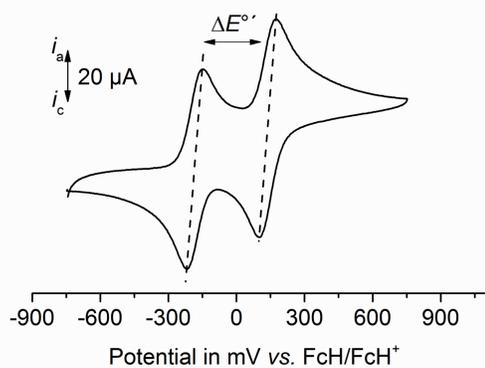
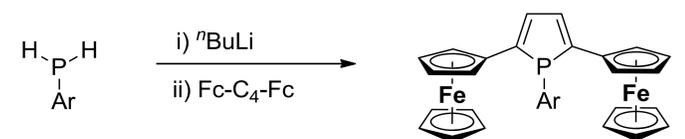
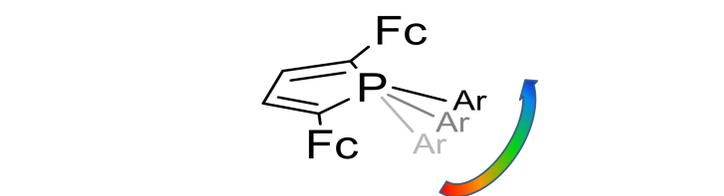
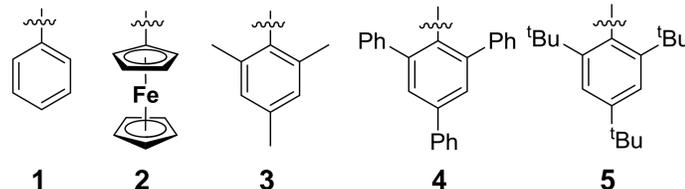


Figure 2. Cyclic voltammogram of **5**; scan rate 100 mV·s⁻¹ at glassy carbon electrode, 1.0 mmol·L⁻¹ solution in anhydrous dichloromethane; 0.1 mol·L⁻¹ [NⁿBu₄][B(C₆F₅)₄] as supporting electrolyte; 25 °C.

The ferrocenyl units of **1–5** could be oxidized separately showing two (**1,3–5**) or three (**2**) reversible redox processes. The increase of the redox splittings in this series **1** (280) \approx **2** (265) $<$ **3** (295) $<$ **5** (315) $<$ **4** (340) may indicate a higher electronic interaction for the ferrocenyls in phospholes with the bulky electron-donating groups bonded to the P atom (Table 3).



Scheme 1. Synthesis of phospholes **1–5**, Fc = Fe(η^5 -C₅H₅)(η^5 -C₅H₄).



The concept of the planarization of the pyramidal phosphorus environment with sterically demanding substituents at phosphorus was applied to 2,5-diferrocenyl substituted phospholes.

Table 3. NIR and CV data of **1–5**.

	ΔE° (mV)	ν_{\max} (cm ⁻¹) (ϵ_{\max} (L·mol ⁻¹ ·cm ⁻¹))	$\Delta \nu_{1/2}$ (cm ⁻¹)
1 ^[4]	280	5000 (1750)	3050
2	265	4850 (1850)	3250
3	295	4900 (2750)	2700
4	340	4650 (2650)	2800
5	315	5050 (3000)	2550

A flattening of the phosphorus pyramidal environment caused by the steric strain of the P-bonded substituent enhances the coupling between the ferrocenyl units in 2- and 5-position. All molecules can be classified as class II systems according to Robin and Day.^[5]

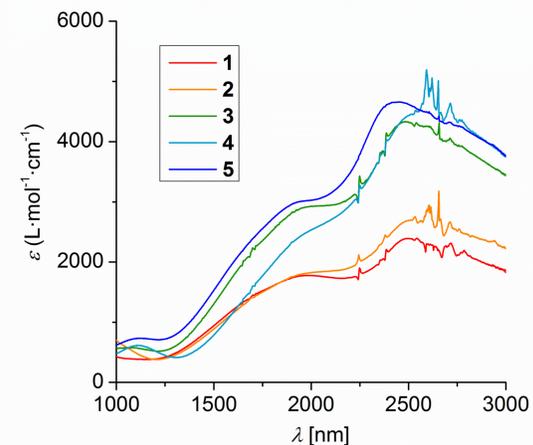


Figure 3. UV-vis/NIR spectra of [1]⁺–[5]⁺ at 25 °C in dichloromethane (2.0 mmol·L⁻¹) supporting electrolyte [NⁿBu₄][B(C₆F₅)₄].

Conclusion

In order to planarize the pyramidal phosphorus environment, 2,5-diferrocenyl-phospholes **1–5** with increasing sterically demanding substituents have been synthesized. An increase of the steric demand results in a more planar geometry around the phosphorus atom as demonstrated by X-ray diffraction and VT-NMR studies. Electrochemical and spectroelectrochemical investigations showed that the flattening of the phosphorus environment increased the interactions between the ferrocenyl units in 2,5 position, which might be attributed to a better delocalization within the phosphole motif.

References and Acknowledgement

- [1] For example: (a) A. Hildebrandt, D. Schaarschmidt, R. Claus, H. Lang, *Inorg. Chem.* **2011**, *50*, 10623-10632. (b) A. Hildebrandt, H. Lang, *Organometallics* **2013**, *32*, 5640-5653. [2] D. B. Chesnut, L. D. Quin, *Heteroat. Chem.* **2007**, *18*, 754-758. [3] L. D. Quin, *Curr. Org. Chem.* **2006**, *10*, 43-78. [4] D. Miesel, A. Hildebrandt, M. Korb, P. J. Low, H. Lang, *Organometallics* **2013**, *32*, 2993-3002. [5] R. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247-422.

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