**Introduction**

Recently, we investigated a number of ferrocenyl-substituted 5-membered heterocycles regarding the electronic interaction between the Fe/C-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 dentic system.\(^2\) A possibility to increase the delocalization within the phosphole ring is the use of sterically demanding substituents bonded to the phosphorous 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 \(\Delta H^\ddagger\), and entropies \(\Delta S^\ddagger\). Compound 5 with the bulky tert-butyl groups exhibits the lowest inversion barrier within this series as demonstrated by a coalescence temperature below \(-100^\circ\text{C}\).

**X-ray Discussion**

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

**Conclusion**

In order to planarize the phosphorous 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 phosphorous atom as demonstrated by X-ray diffraction and VT-NMR studies. Electrochemical and spectroelectrochemical investigations showed that the flattening of the phosphorous environment increased the interactions between the ferrocenyl units in 2.5 position, which might be attributed to a better delocalization within the phosphole motif.

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