

Synthesis of Transition Metal Complexes with Tuneable N6-Coordination Sphere

*Silvio Heider and Holm Petzold**

Chemnitz University of Technology, Institute of Chemistry,

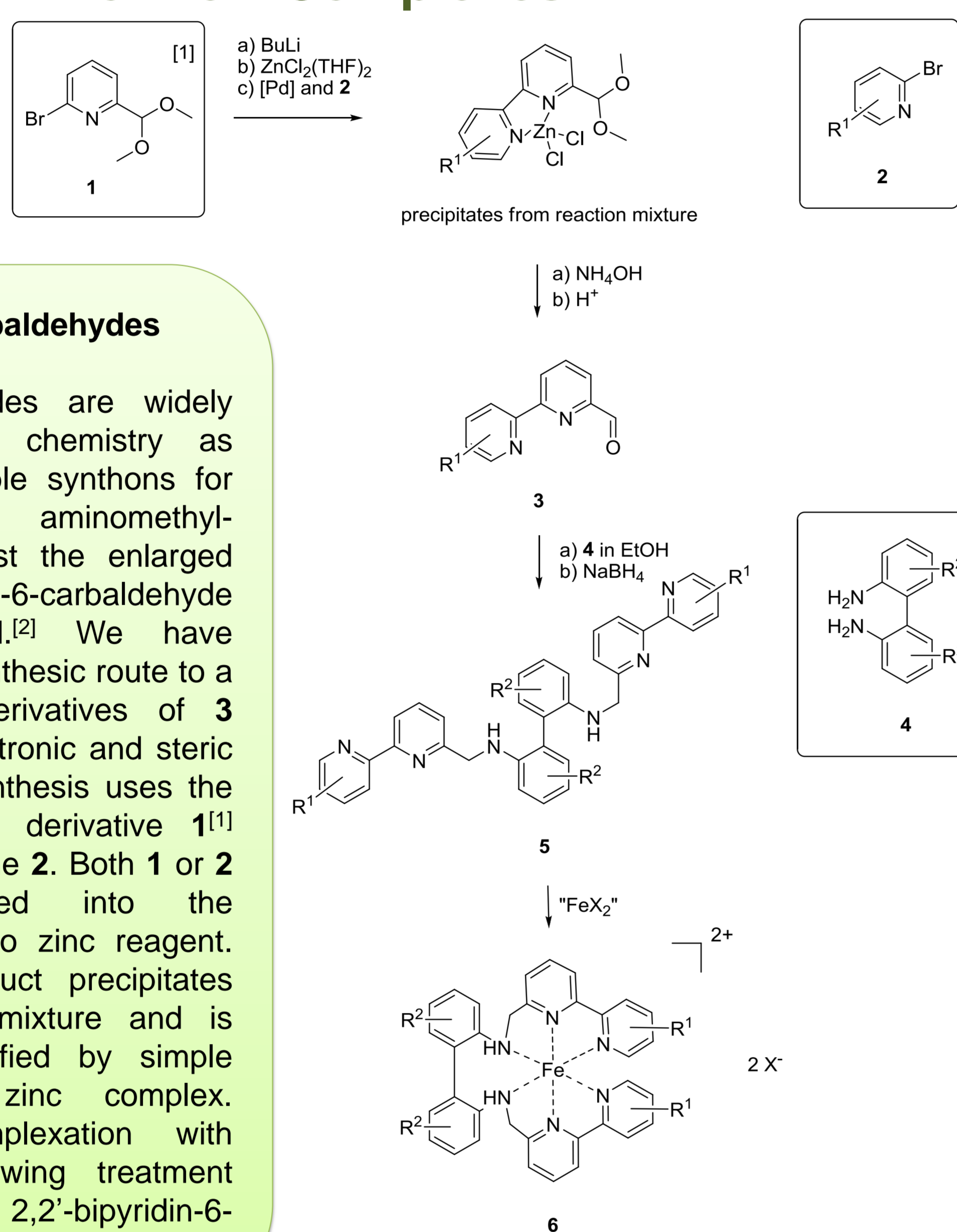
Department of Inorganic Chemistry, Straße der Nationen 62, 09111 Chemnitz, Germany

Dr. Holm Petzold; phone: +49(0)371 531 37463, email: holm.petzold@chemie.tu-chemnitz.de

Introduction

Transition metal complexes have unique properties due to their open d shell. To make use of them in new materials for data storage, sensors or new displaying technologies precise tuning of the ligand field strength is essential. Among the vast amount of described ligands in transition metal complexes the good π -acceptor polypyridyl ligands like 2,2'-bipyridine and 2,2':6',2''-terpyridine derivatives are among the most popular, however, synthesis of those ligands is still a challenge. We have used Negishi cross coupling to obtain 2,2'-bipyridyl-6-aldehydes **4** using the easily available asymmetric pyridine derivative **1**.^[1] The high yield in the Negishi cross coupling allows the efficient introduction of the second pyridine ring from a bromopyridine **2** in a late step of the synthesis. Aldehydes **3** have been employed in the synthesis of polypyridylamines **5**.^[2] The tuning of the ligand field strength in the transition metal complexes employing **5** as ligands was demonstrated on Fe²⁺ spin crossover (SCO) complexes **6**. Using Aldehydes **3** and di-, tri- or tetraaminoaryl derivatives allows the expansion to polynuclear complexes with interacting Fe²⁺ SCO centers.

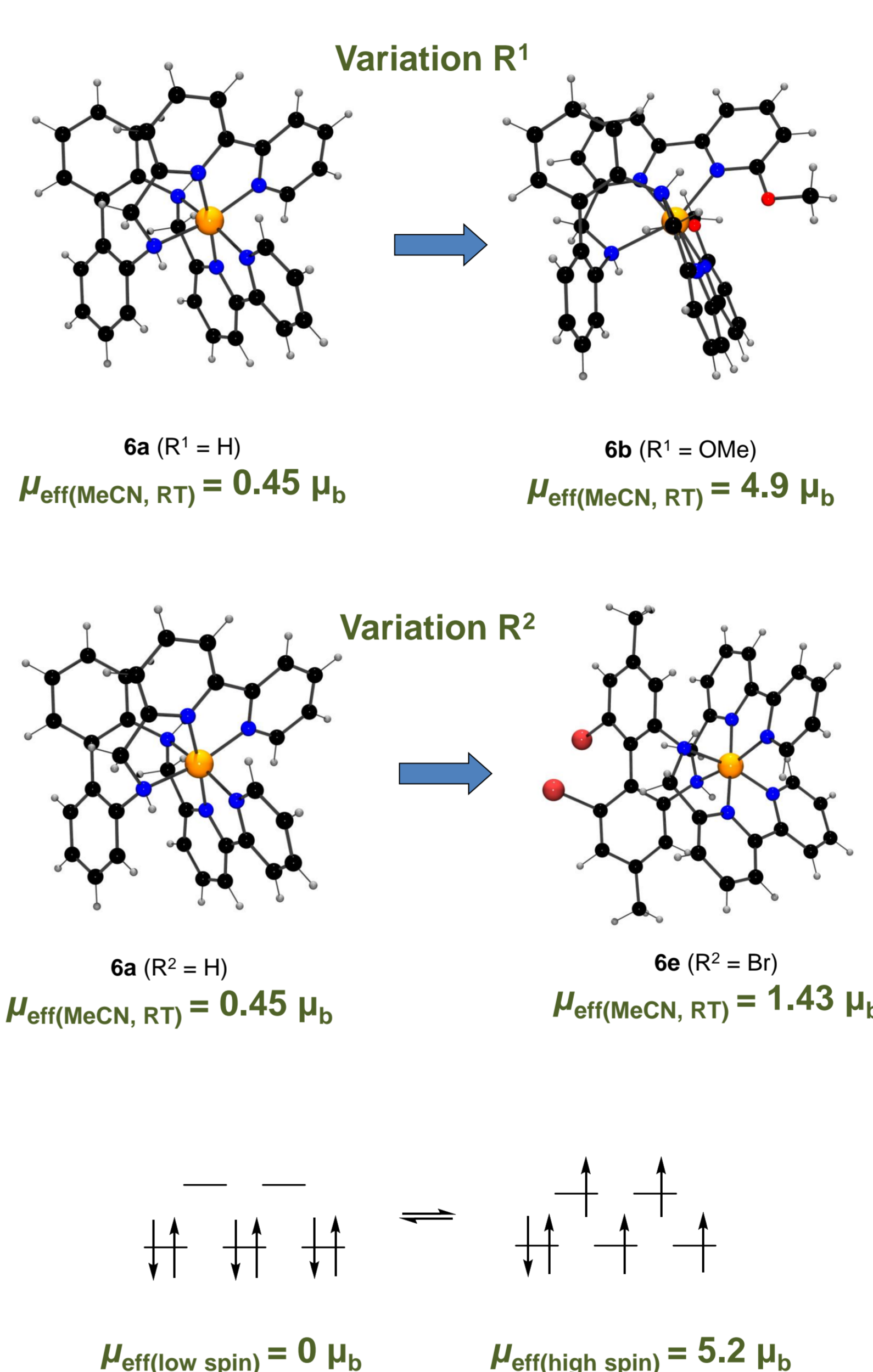
Construction of the N6-Donor Ligand Scaffold for Fe²⁺ Complexes^[3]



2,2'-Bipyridin-6-carbaldehydes

Pyridyl-2-carbaldehydes are widely used in inorganic chemistry as commercially available synthons for pyridylimines and aminomethylpyridines. In contrast the enlarged synthon 2,2'-bipyridyl-6-carbaldehyde **3** is rarely used.^[2] We have elaborated a new synthetic route to a broad range of derivatives of **3** allowing to tune electronic and steric effects in **3**. The synthesis uses the asymmetric pyridine derivative **1**^[1] and a 2-bromopyridine **2**. Both **1** or **2** can be converted into the corresponding organo zinc reagent. The protected product precipitates from the reaction mixture and is separated and purified by simple filtration of the zinc complex. Subsequent decomplexation with ammonia and following treatment with acid yields 2,2'-bipyridin-6-carbaldehydes **3**.

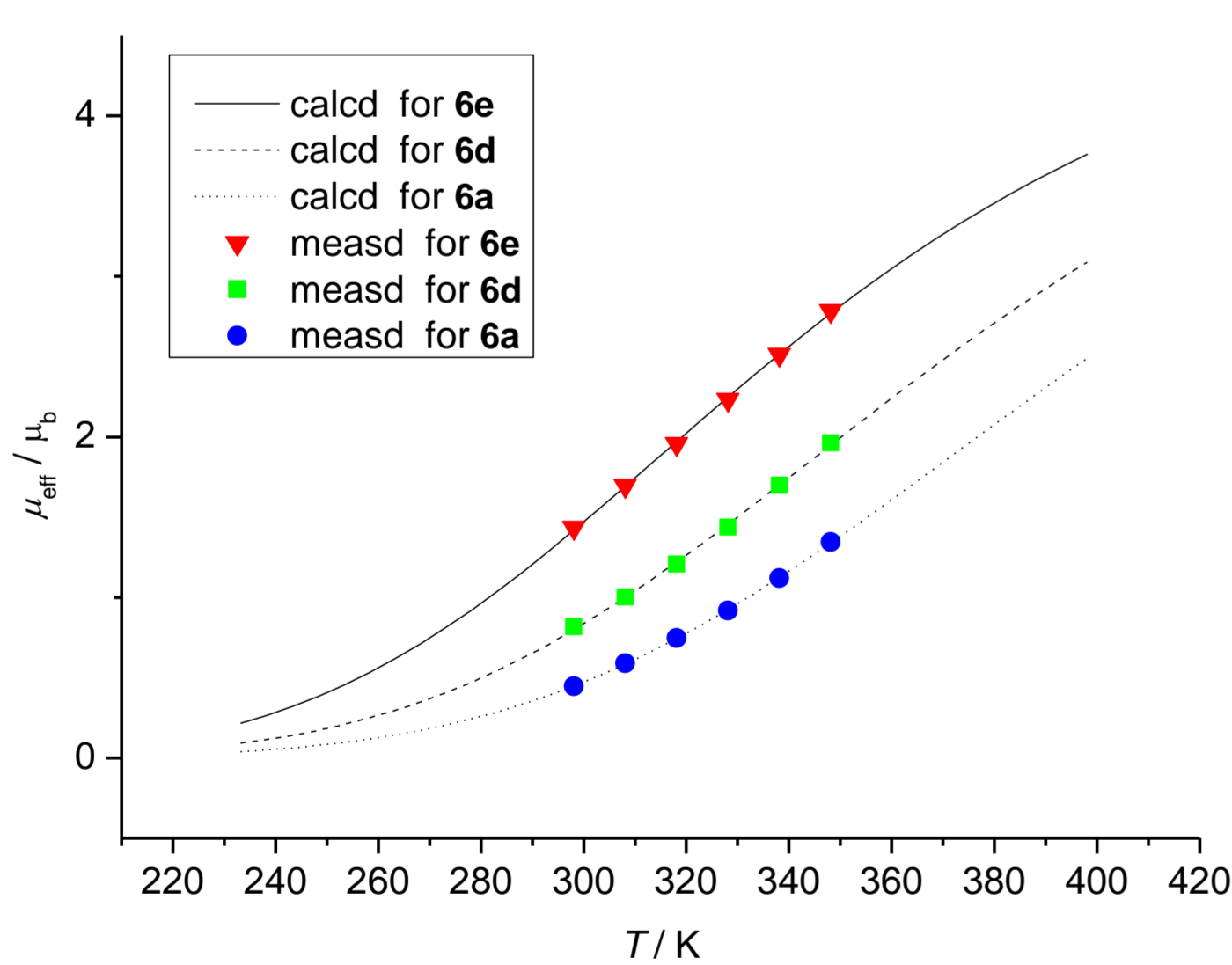
The Fe²⁺ Complexes^[3]



6 (R ¹ @ 6'-bipy)	Fe-N (Å) _{min/max} (solid @ 110K)	HS/LS (solid @ 110K)
6a (H)	1.883(4)-2.059(4)	LS
6b (OMe)	2.1067(18)-2.292(2)	HS
6c (Me)	2.1089(14)-2.2995(15)	HS

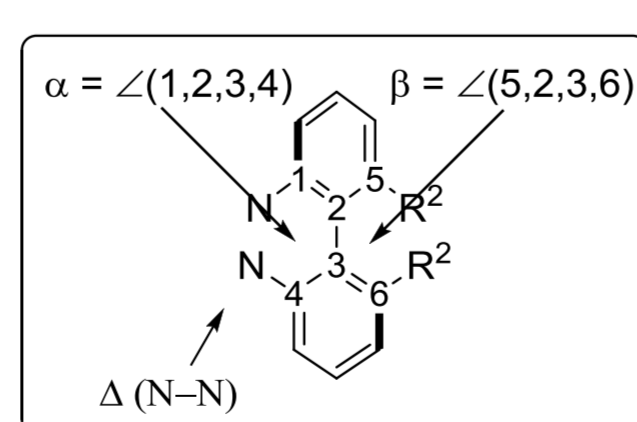
6 (R ² @ 6/6'-biphenyl)	Fe-N (Å) _{min/max} (solid @ 110K)	HS/LS (solid @ 110K)
6a (H)	1.883(4)-2.059(4)	LS
6d (Me)	1.903(2)-2.071(2)	LS
6e (Br)	1.883(2)-2.068(2)	LS

Tuning of SCO Transition^[3]

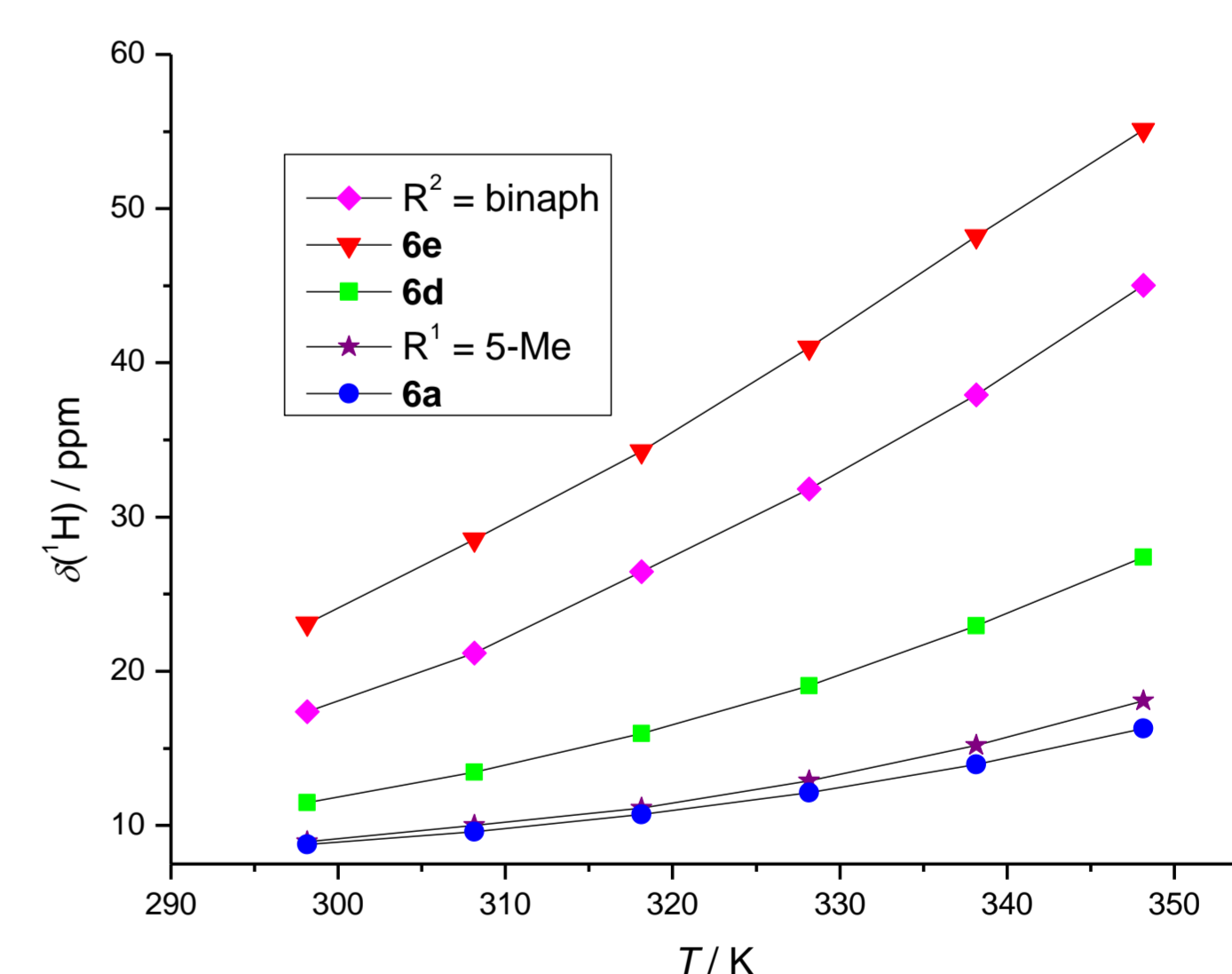
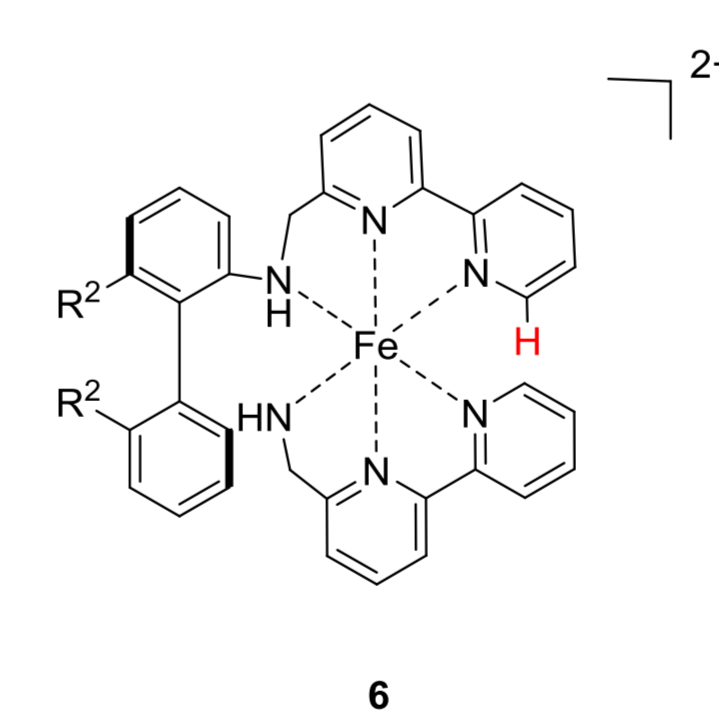


6 (T _{1/2})	$\Delta(N-N)$ (Å) (solid @ 110K)	$\Delta(\alpha-\beta)$ (solid @ 110K)
6a (341 K)	3.0068(62)	2.8(10)°
6b (HS)	3.3556(29)	1.1(4)°
6c (HS)	3.3192(22)	1.6(3)°
6d (375 K)	3.0304(32)	5.0(4)°
6e (403 K)	3.0607(31)	7.8(4)°

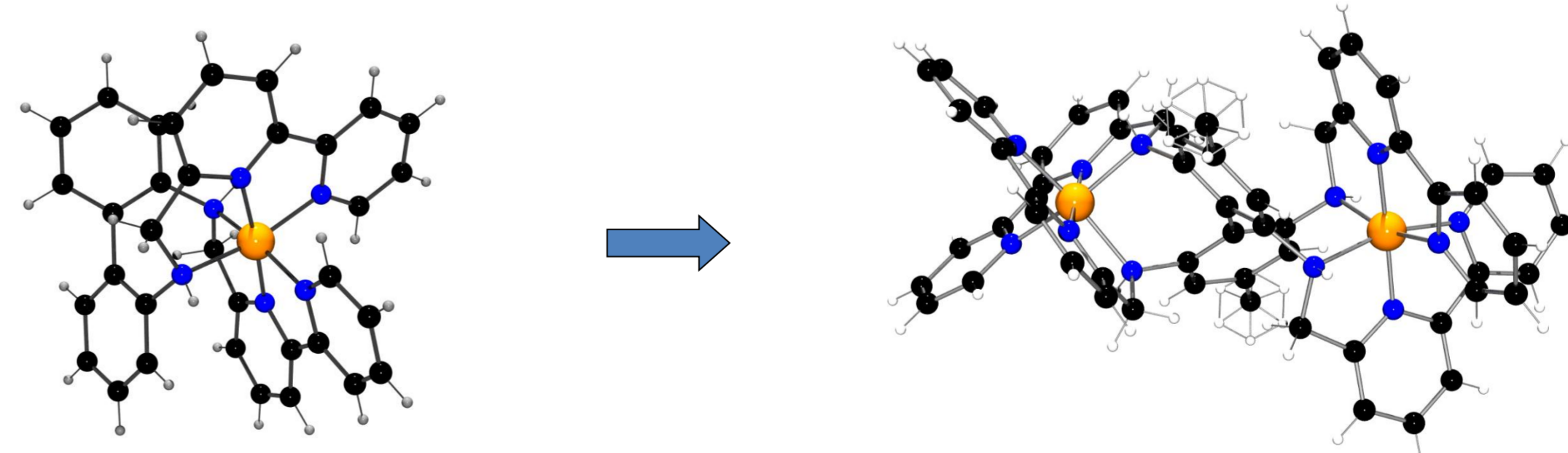
For Fe²⁺ complexes **6a** (R² = H), **6d** (R² = Me) and **6e** (R² = Br) the magnetic moments were determined in MeCN solution using Evans' method. The measured data was fitted to a regular solution model yielding the ΔH , T_{1/2} and subsequently ΔS . For all complexes ΔS was obtained about 56 J·mol⁻¹·K⁻¹, significantly different is ΔH (19.1 kJ·mol⁻¹ (**6a**), 20.6 kJ·mol⁻¹ (**6d**) and 22.5 kJ·mol⁻¹ (**6e**)). A correlation between torsion of the biphenyl bridge in solid state and T_{1/2} is found. Currently we are expanding this system to a dinuclear complex **7** that could probably show a positive cooperativity of two Fe²⁺ SCO centers in solution.^[4]



Probing Spin State by ¹H-NMR^[3]



Coming soon^[4]



Conclusion

In summary, we have used 2,2'-bipyridin-6-carbaldehydes **3** for the synthesis of polypyridylamines **5**, that are employed as ligands in Fe²⁺ spin crossover complexes **6**. The used different bridges **4** allow the direct tuning of the spin transition temperature T_{1/2} of the SCO complexes **6** by steric effects.^[3]

References

- [1] R. G. Hicks, B. D. Koivisto, M. T. Lemaire, *Org. Lett.* **2004**, 6, 1887-1890.
- [2] a) E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuberger, S. Schaffner, *Dalton Trans.* **2009**, 8165-8167; b) L. J. Baird, C. A. Black, A. G. Blackman, *Polyhedron* **2007**, 26, 378-384; c) E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuberger, J. A. Zampese *Eur. J. Inorg. Chem.* **2010**, 2000-2011; d) E. C. Constable, G. Zhang, C. E. Housecroft, M. Neuberger, J. A. Zampese *Chem. Commun.* **2010**, 3077-3079; e) E. C. Constable, G. Zhang, C. E. Housecroft, J. A. Zampese *Dalton Trans.* **2010**, 5332-5340.
- [3] H. Petzold, S. Heider, *Eur. J. Inorg. Chem.* **2011**, DOI: 10.1002/ejic.201001139.
- [4] S. Heider, H. Petzold, unpublished, suggested by solution-¹H-NMR.

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