

Summary

The aim of this thesis was the synthesis of paramagnetic nickelocene compounds with a face-to-face arrangement and the evaluation of the magnetic coupling mechanism.

A synthetic route to disodium 1,8-(dicyclopentadiendiyl)naphthalene **5** has been demonstrated starting with 1,8-diiodonaphthalene **1**. The substitution of the diiodo functions with cyclopentadienyl substituents yields the *Diels-Alder* product **5**. In a subsequent *retro-Diels-Alder* reaction the disodium salt **5** forms, which is a very useful precursor for different cobalt and vanadium complexes synthesized in the Heck group ever since.

A synthesis to the first head-to-head stacked paramagnetic nickelocene 1,8-bis-[(pentamethyl- η^5 -cyclopentadienyl)(η^5 -cyclopentadiendiyl)-nickel(II)]naphthalene (**6**) starting with disodium salt **5** has been reported.

CV experiments demonstrate four one electron transfers, which are only partly resolved. The first and the second oxidation steps seem to be electrochemically reversible whereas the third redox couple is only partially reversible and the fourth one is chemically irreversible. The peak separation $\Delta E_{1/2}(2-1)$ is only 128 mV, which is characteristic for a weak metal-metal interaction, so that compound **6** belongs to group II of the *Robin-Day* classification.

X-ray structure analysis shows an intermolecular face-to-face arrangement of the Cp* ligands to their neighbor molecules in the crystal.

Solid state magnetic properties of the bisnickelocene complex **6** was successfully rationalized through a combination of structure analysis and broken symmetry DFT calculations. Additional measurements of the isolated molecules by doping experiments are in good agreement with these results.

SQUID experiments in solid state display antiferromagnetic behaviour with a Néel - temperature of 101 K, a coupling constant $J = -31.49 \text{ cm}^{-1}$ and a g -value $g = 1.813$. The antiferromagnetic coupling in the pure sample is slightly bigger compared to the diluted sample which is attributed to an intermolecular antiferromagnetic coupling. This interaction is much weaker than the intramolecular one.

The theoretical evaluation of the intramolecular interaction in the bisnickelocene **6** yields in two main exchange pathways: 1. The direct overlap of the face-to-face Cp-ligands of the nickelocene moiety leads to a type of superexchange; 2. The through bond interaction via the naphthyl backbone leads to ferromagnetic coupling, which is only very small and overshadowed by the much stronger antiferromagnetic coupling. Broken symmetry DFT calculations of the electronic structure of complex **6** reveals a singlet ground state, which is in agreement with the experimental data.

Oxidation of compound **6** with ferrocenium tetrafluoroborate yielded the dikation **8**. The paramagnetic ^1H NMR shift range amounts only half of the neutral compound **6**, which can be explained with the lower number of unpaired electrons. VT ^1H NMR spectroscopy in solution between -90 and 20° shows *Curie* behavior. Magnetic measurements in solid state results in a very weak antiferromagnetic coupling with 2 K, a coupling constant $J = -1.24 \text{ cm}^{-1}$ and a g -value $g = 1.806$. These results are in agreement with the data of the corresponding cobalt compound recently published from our group.

The attempt of the synthesis of unsubstituted 1,8-bisnickelocenyl-naphthalene with disodium salt **5** and the $[\text{Cp}_3\text{Ni}_2][\text{BF}_4]$ tripledecker as CpNi transfer reagent yielded instead the *ansa*-nickelocene **21**. The mechanism is still unknown, but a dismutation was discussed. A similar dismutation reaction has been reported.[133] To illustrate the interplay between the arrangement of the nickelocene units in the solid state

structure and the magnetic behavior related to the intermolecular interactions the magnetic properties of the ansa-nickelocene **21** was investigated. In this context a more targeting synthesis could be established.

The magnetic measurements show an antiferromagnetic interaction with a Néel-temperature of 25 K. The experimental data has been simulated, with the assumption of a magnetic dimer and yields a coupling constant $J = -10.07 \text{ cm}^{-1}$ and a g value of $g = 2.029$. The crystal structure analysis demonstrates this dimeric arrangement with a nickel-nickel distance of only 521 pm and the shortest nickel-carbon distance of 393 pm. In order to evaluate this intermolecular magnetic interaction attributed to crystal packaging, diluted samples of **21** in a diamagnetic ruthenium host **22** were investigated by SQUID measurements. The susceptibility as a function of the temperature shows a rising graph without a maximum. These results are in agreement with the intermolecular coupling as the main mechanism of the magnetic interaction. However, the effective magnetic moment as a function of the temperature shows a decreased magnetic moment under 10 K. To investigate whether a singlet-triplet transition could be the reason, DFT calculation were performed. The distortion of the molecule due to the naphthyl bridge yields a splitting of the two SOMO of 15kJ/mol, but calculations on the electronic ground state reveal a triplet ground state to be most favorable.

Oxidation of compound **21** with ferrocenium tetrafluoridoborat yielded the 1,1'-(naphthalin-1",8"-diyl)-nickelocenium tetrafluoridoborate. **23** VT ^1H NMR spectroscopy in solution between -90 and 20 °C illustrates Curie behavior. The splitting of the former e_g -orbitals caused by the bent structure, enables ESR spectroscopy of complex **23** already at 100 K with the g -values $g_1 = 1.868$, $g_2 = 2.008$ and $g_3 = 2.050$. These results are in agreement with the data of the isoelectronic cobalt complex recently investigated in our group.

VT ^1H NMR spectroscopy in solution between 190 and 290 K demonstrates *Curie*-behavior, but SQUID-measurements in solid states result in a very strong antiferromagnetic interaction with a Néel-temperature over 400 K. This coupling can be attributed to the onedimensional stacking of the nickelocenium moiety in the crystal, presumably yielding in a superexchange which leads to the antiferromagnetic interaction. In this thesis the differences between intramolecular and intermolecular magnetic interactions have been demonstrated by four paramagnetic nickel-compounds. The enormous importance of the knowledge of the crystal structure for the evaluation of the magnetic coupling mechanism could be shown.

The iron-nickel compounds 1-[(pentamethyl- η^5 -cyclopentadienyl)(η^5 -cyclopentadiendiyl)nickel(II)]-8-ferrocenylnaphthalene (**11**), 1-nickelocenyl-8-ferrocenylnaphthalene (**12**), 1,1'-bis(-8-ferrocenyl-1-naphthyl)nickelocene (**13**) and 1,1'-bis[(pentamethyl- η^5 -cyclopentadienyl)(η^5 -cyclopentadiendiyl)nickel(II)]-8,8'-naphthyl]ferrocene (**14**) could be synthesized, but due to the instability of the nickelocene moiety against silica and aluminiumoxide, chromatography led to decomposition and the products could not be purified. Therefore no magnetic interactions were investigated.