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Ferrocene–Mn^{II} π-interaction in the complex $[Fc_2Bpz_2^{Ph}Mn(THF)Cl]$

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ABSTRACT

The ferrocene-based bis(pyrazol-1-yl)borate ligands $[Fc_2Bpz_2]^-$ (**[2]**$^-$) and $[Fc_2Bpz_2^{Ph}]^-$ (**[2^{Ph}]**$^-$) have been prepared (Fc: ferrocenyl; pz: pyrazol-1-yl; pz^{Ph}: 3-phenylpyrazol-1-yl). Treatment of **[2]**$^-$ and **[2^{Ph}]**$^-$ with $MnCl_2$ in THF leads to the complexes $[Fc_2Bpz_2Mn(THF)(\mu\text{-}Cl)_2Mn(THF)pz_2BFc_2]$ (**3**) and $[Fc_2Bpz_2^{Ph}Mn(THF)Cl]$ (**3^{Ph}**), respectively, which have been structurally characterized by X-ray crystallography. While there is clearly no ferrocene–Mn^{II} π-coordination in the solid-state structure of **3**, short Mn^{II}–C_5H_4 contacts are established in **3^{Ph}** (shortest Mn–C distances: 2.780(2) Å, 2.872(2) Å). The cyclic voltammograms of **K[2^{Ph}]** and **3^{Ph}** show the first ferrocene/ferricinium redox wave of **3^{Ph}** to be shifted anodically by 0.60 V compared with the first Fe^{II}/Fe^{III} transition of **K[2^{Ph}]**.

1. Introduction

The structural motif of a multiple-decker sandwich complex is ideally suited to bring about electronic communication between the constituent metal ions. This has been impressively demonstrated by Siebert et al. who prepared an organometallic semiconductor based on an extended columnar structure consisting of Ni ions and η^5,μ-2,3-dihydro-1,3-diborolyl ligands [1–3]. For practical reasons, it would, however, be desirable to substitute simple cyclopentadienyl ligands for the sophisticated boron heterocycle. Numerous triple-decker sandwich complexes of the permethylated cyclopentadienyl derivative $[C_5Me_5]^-$ have already been isolated and structurally characterized [4]. In contrast, the number of known examples featuring exclusively the unsubstituted $[C_5H_5]^-$ ligand is still rather small (e.g. $[Ni_2(C_5H_5)_3]^+$ [5], $[Tl_2(C_5H_5)_3]^-$ [6]).

Research in our group is focused on heterobimetallic multiple-decker sandwich complexes consisting of ferrocene and bridging metal ions M^{n+} (**A**; Fig. 1). Oligonuclear as well as polymeric species **A** are known in which M^{n+} is an alkali metal ion [7–14]. Multiple-decker complexes of ferrocene have also been obtained with the group III metal ions Ga^+ and Tl^+ [15–17]. Two structurally characterized **A**-type complexes with M^{n+} being a transition metal ion are the polymeric Ag-complex **B** [18] and the Zn-complex **C** [19] (Fig. 1).

From these examples it becomes evident that chances to observe ferrocene–metal π-interactions are highest when donor solvents can be avoided during complex synthesis. Moreover, if the sandwich complex bears a positive charge, weakly coordinating counteranions are to be selected. In the case of the transition metal species **B** and **C**, the π-interactions are supported by chelating sidearms stabilizing the desired multiple-decker sandwich structure.

The purpose of this paper is to report on a novel class of ferrocene-based ligands that have been specifically designed to maximize the chance for ferrocene–metal π-coordination. As a proof-of-principle, the synthesis and structural characterization of the first ferrocene–Mn^{II} multiple-decker sandwich complex will be presented.

2. Results and discussion

For a more general approach to ferrocene-containing multiple-decker sandwich complexes it is necessary to have the option to use transition metal salts that require strongly coordinating solvents as reaction media. Moreover, we want to establish multiple-decker sandwich motifs not only in the solid state but also in solution. Given this background, the design of ferrocene ligands **K[2]** and **K[2^{Ph}]** (Scheme 1) is based on the following considerations: (i) similar to **B** and **C**, a chelating sidearm should be present, (ii) bis(pyrazol-1-yl)borates are a good choice as supporting ligands, because they offer *two* donor sites and, in addition, attract the metal cation electrostatically, and (iii) the incorporation of two ferrocenyl moieties in the ligand molecule will increase the

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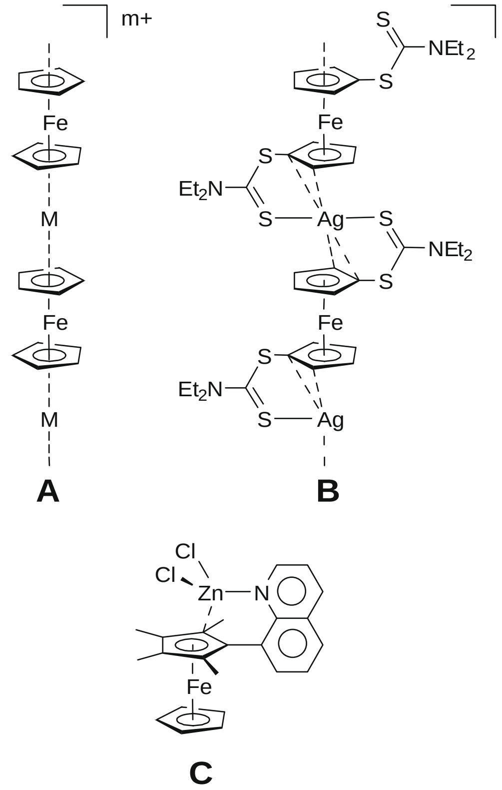
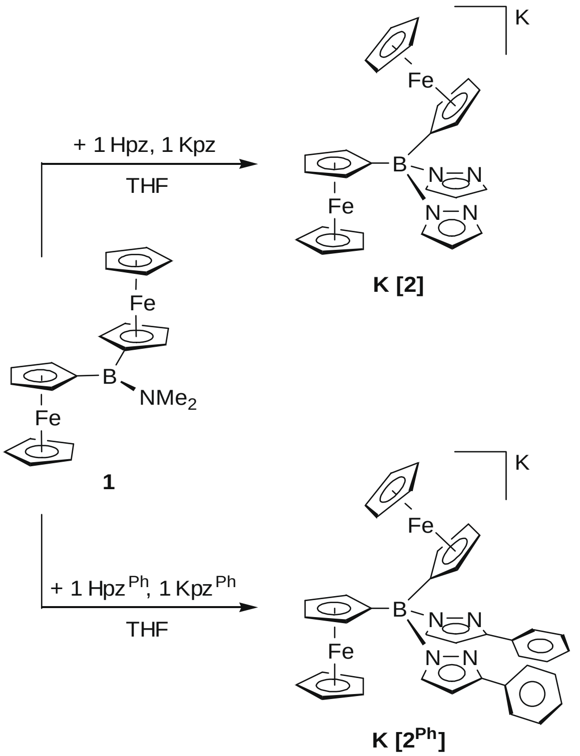


Fig. 1. General structure of a ferrocene-based heterodinuclear multiple-decker sandwich complex **A**; representation of the **A**-type silver complex **B** and of a related zinc complex **C**.

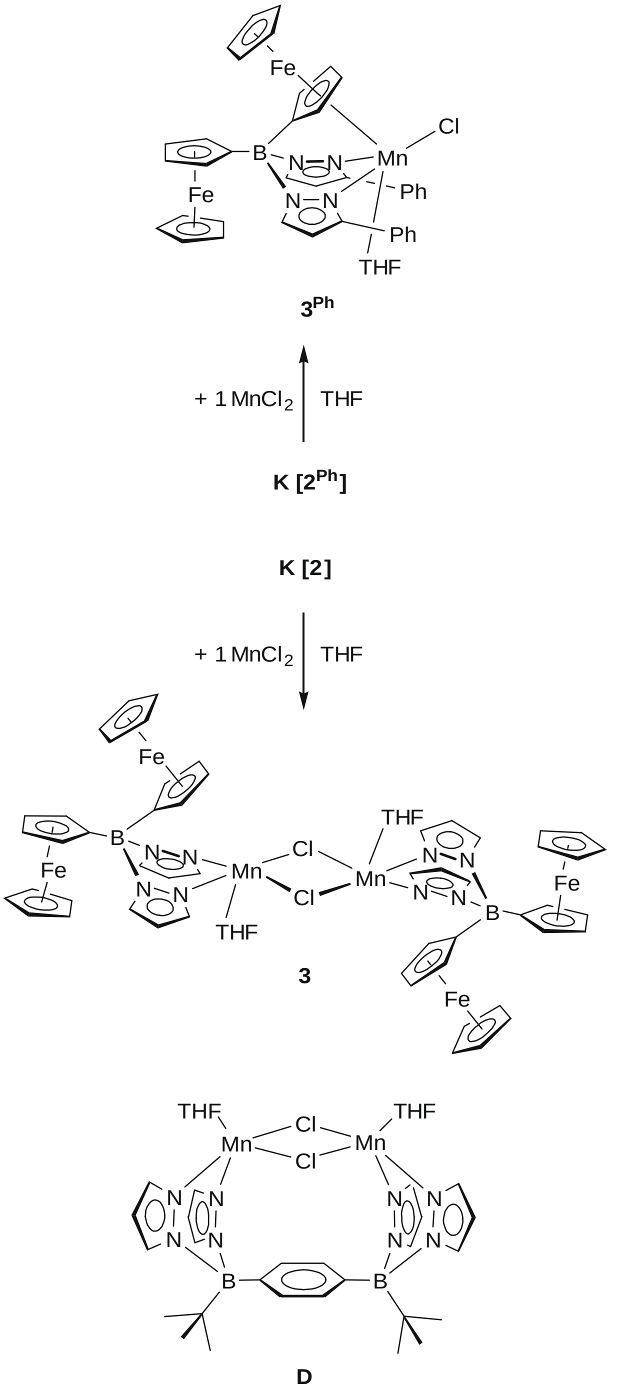


Scheme 1. Synthesis of the ferrocenyl-substituted bis(pyrazol-1-yl)borate ligands **K[2]** and **K[2^{Ph}]**.

number of conformations that have the potential to bring about ferrocene–metal π-coordination.

2.1. Synthesis and spectroscopical characterization

The ligands **K[2]** and **K[2^{Ph}]** (Scheme 1) were synthesized by treatment of the aminoborane **1**[12] in THF with a mixture of Hpz/Kpz and Hpz^{Ph}/Kpz^{Ph}, respectively (Hpz: pyrazole; Hpz^{Ph}: 3-phenylpyrazole). Heating at reflux temperature for several hours is required to drive the transamination reaction to completion.



Scheme 2. Synthesis of the Mn^{II} complexes **3** and **3^{Ph}** of the ligands **[2]**$^-$ and **[2^{Ph}]**$^-$; representation of compound **D** used for comparison.