



Exploring the coordination chemistry of *O,N,O'*-ligands modified by 2-thienyl-substituents to nickel



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ABSTRACT

The coordination chemistry of 5-hydroxypyrazoline ligand class **1** modified by 2-thienyl substituents with Ni(OAc)₂ and DMAP as co-ligand to form the nickel complexes **4** [Ni(1-2H)(dmap)_x] was investigated. The complexes were characterized and investigated by various techniques, pointing out different complex geometries, octahedral vs. square planar, depending on the connectivity of the 2-thienyl substituent. In more detail, X-ray crystallography revealed an *O,N,O'*-coordination in which the ligand is planar and the other coordination sites on the nickel center are occupied by one or three DMAP co-ligands, respectively. Moreover, the complexes have been applied as precatalyst in nickel-catalyzed hydrodeacylation reactions.

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Catalysis is one of the key methods for the development of sustainable, efficient, and selective processes [1]. In this regard, metal catalysis turned out to be an excellent toolbox for such purposes [2]. In more detail, the properties or performance of the catalyst is strongly influenced by ligands [3]. Based on that, the design of new ligands and the study of their coordination chemistry are important research aims [4]. Moreover, the inexpensiveness, great availability, easy synthesis, high tunability, high flexibility and stability of the ligands should be considered. With respect to these requirements an interesting motif can be the ligand class **1**, which is easily accessible, starting from commercially available chemicals (Fig. 1). Recently, the coordination chemistry of ligand class **1** was studied and different coordination modes were observed, depending on the metal and the added co-ligands (e.g., *O,N,O'*; *O,N*; *O,O'*; and *N,O'*). For instance, reacting **1** with ZnMe₂ revealed an *O,O'*-coordination after deprotonation [5]. Interestingly, the addition of a base (TMEDA) to the complex allowed the second deprotonation and created a seven-membered ring system. Furthermore, the reaction of Mo₂(O^tBu)₆ with ligand class **1** showed *O,O'*-coordination and was a useful precatalyst for the reduction of organic amides to amines [6]. In contrast to that, an *N,O'*-coordination was observed, when ligand class **1** was reacted with Cu(OAc)₂ and triphenylphosphane as co-ligand. Interestingly, the copper complex was a useful precatalyst in the copper-catalyzed amination of C–H bonds [7]. Moreover, the reaction of ligand class **1**

with Ni(OAc)₂·4H₂O and 4-dimethylaminopyridine (DMAP) resulted after double deprotonation in the formation of an octahedral complex with an *O,N,O'*-coordination (Fig. 1, A), while in the presence of ammonia or phosphane co-ligands a square planar geometry was observed (Fig. 1, B) [8]. Interestingly, various applications as precatalysts have been reported, e.g., C–C cross-coupling reactions, hydrodehalogenations, hydrodeacylations [9]. It is noteworthy that, the structural appearance of the complexes (octahedral vs. square planar geometry) strongly depends on the added co-ligands and the control of the geometry by the tridentate ligand was not studied so far (Fig. 1). Based on that, we report herein on the synthesis and characterization of 5-hydroxypyrazoline ligands modified by 2-thienyl substituents, which allow the control of the geometry at the nickel center (Fig. 1, D–F). Moreover, the potential of the complexes was studied in the hydrodeacylation reactions.

The ligands **1a–c** were synthesized in accordance with methods reported in the literature [10]. In more detail, the corresponding hydrazides were refluxed with substituted acetyl acetones in methanol obtaining ligand class **1** after work-up as crystalline compound (Scheme 1). In agreement to earlier works, for ligand **1a** the cyclic 5-hydroxypyrazoline form was obtained as proven by NMR investigations [¹H NMR δ = 3.34–3.63 ppm (m, CH₂)] and single-crystal X-ray diffraction analysis (Fig. 2a) [11]. The analytical and structural data are comparable to the recently reported ligand **1** (R¹ = Ph, R² = CF₃), showing a minor influence of the 2-thienyl group on the core of the ligand [5a]. In contrast to that for ligand **1b** two different isomers in a ratio of 1:4 were observed in solution by NMR methods [¹H NMR **1b**: δ = 3.29–3.61 ppm (m, CH₂); **1b'**: δ = 4.13 (s, CH₂)], while in the solid state the hydrazone form **1b'**

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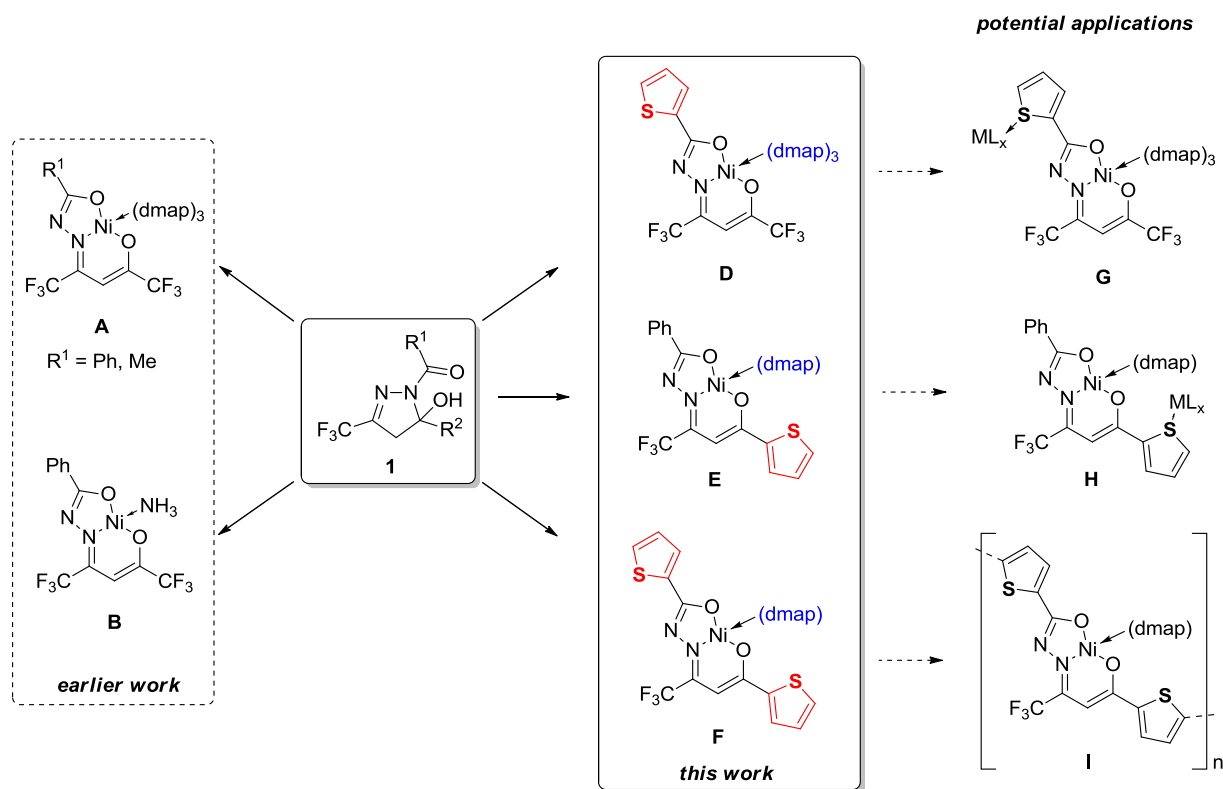


Fig. 1. Coordination modes of ligand class **1** to nickel (dmap = 4-dimethylaminopyridine).

was attained (Fig. 2b). DFT calculations on the B3LYP level of theory and the 6-31G(d) basis set were carried out and revealed a higher stability for the hydrazone form **1b'** of 20 kJ/mol compared to **1b** [12]. Probably the carbonyl function attached to the thienyl group (**1b/1b'**) is less electrophilic than the carbonyl function attached to the electron-withdrawing trifluoromethyl group (**1a**), hence the cyclization is less favored. Moreover, in case of **1c** only the hydrazone form **1c'** was observed by NMR [$^1\text{H NMR } \delta = 4.62 \text{ ppm (s, } \text{CH}_2\text{)}$].

Afterwards, in agreement to our previously established protocol a methanol solution of the ligand and an excess of DMAP were added to a solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in methanol at room temperature [8]. After stirring overnight, all volatiles were removed to obtain brown powders, which were extracted with toluene and purified by crystallization to obtain brown crystals. Crystals suitable for X-ray measurements were grown from toluene by slow evaporation of the solvent at room temperature. The solid-state structures of complexes **4b** and **4c** have been characterized by single-crystal X-ray diffraction analysis. Thermal ellipsoid plots, selected bond lengths and angles are shown in Fig. 3. The tridentate ligand is coordinated in a *O,N,O'*-mode creating a five-membered as well as a six-membered ring system and therefore shielding one side of the metal. In contrast to earlier works only one DMAP ligand is coordinated to the square planar nickel center. The DMAP ligand is *cis*-positioned to the oxygen donors, while the nitrogen of the 5-hydroxypyrazoline ligand is connected to the nickel center in the *trans*-position. Comparing the bond distances of the square planar coordinated complexes **4b** and **4c** with the distances of octahedral coordinated complex **A** ($\text{R}^1 = \text{Ph}$ or Me , $\text{R}^2 = \text{CF}_3$) significant shorter bond lengths were observed. For instance the Ni1-N1 , Ni-O1 , Ni-O2 and Ni1-N3 bond distances are ca. 0.2 Å shorter than those for the complexes **4b** and **4c** (complex **A**: Ni1-N1 : 2.055(3) Å, Ni1-O1 : 2.021(3) Å, Ni1-O2 : 2.041(3) Å, and Ni1-N3 : 2.118(3) Å). In the case of complex **4a** no suitable crystals for X-ray measurements were

obtained. However, a preliminary structure revealed an octahedral geometry as observed for complex **A** with three DMAP ligands along with the tridentate *O,N,O'*-ligand (see supporting information). Based on these observations the C1-substitution in the complexes is crucial for the geometry and the 2-thienyl substituent can influence the geometry by electronic and steric effects. The complexes were also investigated by $^1\text{H NMR}$ spectroscopy, showing broad signals for the paramagnetic compound **4a**, which could be not assigned. In contrast to that, for the diamagnetic complexes **4b** and **4c** a new signal was found at 6.44 ppm for **4b** (in C_6D_6) and 6.13 ppm for **4c** (in CDCl_3), which is assigned as the C–H proton in the six-membered ring. This was further proven by the absence of any signal for the former CH_2 in the ligand **1**. In addition new signals at 2.05 ppm for **4b** (in C_6D_6) and 3.03 ppm for **4c** (in CDCl_3) were observed for the methyl protons of the DMAP ligand. Moreover, the chemical shifts in the $^{19}\text{F NMR}$ for the CF_3 -groups are slightly high-field shifted compared to ligand class **1**. The coordination of the acyl functionality was investigated by IR measurements. The absence of signals in the region $1600\text{--}1725 \text{ cm}^{-1}$ excludes the possibility for a free or coordinated $\text{C}=\text{O}$ functionality in the coordinated ligand. Also strong signals were monitored in the region $1532\text{--}1618 \text{ cm}^{-1}$, which probably can be attributed to the $\text{C}=\text{N}$ functionality. The mechanism for the formation of the complexes is assumed to be similar to that described in an earlier work [8].

Recently a methodology was set up for the nickel-catalyzed hydrodeacylation of organic cyanides with LiBH_4 as hydride source under mild reaction conditions applying nickel complexes with the *O,N,O'*-ligand **1** as precatalyst [9]. In this regard the catalytic abilities of the complexes **4** were studied in the hydrodeacylation of anisonitrile with LiBH_4 as hydride source (Scheme 2). Interestingly for all complexes excellent yields were realized within 24 h, while within 1 h a higher yield was observed for complex **4b**.

In summary we have investigated the coordination chemistry of 5-hydroxypyrazoline ligand class **1**, modified by 2-thienyl substituents

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