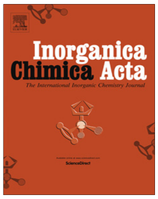
Inorganica Chimica Acta 433 (2015) 3–12

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Carbonyl group coordination preferences in square-planar Ni^{II} and Pd^{II} complexes of pentadentate ligands by electron-withdrawing/donating substituents

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ARTICLE INFO

Article history:
Received 26 February 2015
Received in revised form 20 April 2015
Accepted 27 April 2015
Available online 7 May 2015

Keywords:
Ni^{II} complexes
Pd^{II} complexes
Trifluoromethyl group
Chiral switches
Coordination modes
Density functional theory

ABSTRACT

A series of chirally switchable Ni^{II} and Pd^{II} complexes were synthesized and fully characterized by X-ray crystallography and additionally by NMR. It was found that control of the stereochemical preference between (S^*,S^*) and (S^*,R^*) diastereomers by substituent modification of the ligand sidearms was possible in the process of crystallization with the preferred coordination of the sidearms generally consistent with expectations based on the electron-donating or -withdrawing properties of the sidearm substituent groups. There were however, quite interesting and unanticipated exceptions counter to chemical intuition and it seems that only for complexes with *ortho* substituents are strong preferences for the coordination manner necessarily displayed in the solid state based on the electron-withdrawing or -donating properties of the substituents.

1. Introduction

Molecules that can form supramolecular assemblies frequently possess useful chemical and physical properties [1], and amongst these coordination compounds are particularly prominent since one of the major challenges is to attain a fine balance between structural predictability and coordination flexibility, thereby allowing the compounds to be responsive to external stimuli [2]. In this respect, one successful approach has been the application of ligands containing carbonyl groups specifically intended to be weakly coordinating [3]. We previously introduced a molecular system based on the coordination of achiral pentadentate ligands with d^8 metals [4], and have since extended it to chiral ligands [5]. Such chirally facile interconverting systems have been adopted recently for their potential application as molecular switches [6], though the authors drew attention to the inherent drawback in that no chemical reaction can proceed with 100% conversion [4a]. This is countered however, by the plethora of potential systems that could be applied for such purposes [6].

In our system consisting of square-planar Ni^{II} or Pd^{II} complexes (Scheme 1), two elements of chirality are present: the stereogenic center resulting from the fixation of the chirality at the benzylamine nitrogen and the stereogenic axis arising from the restricted rotation of the non-coordinated *N*-(*o*-benzophenone) amide moiety about the N–C bond. Four species altogether, discounting enantiomers, are possible when utilizing differently substituted sidearms of the ligand and facile interconversion could conceivably occur between two preferred species. For example, the switch between diastereomers (S^*,S^*) and (S^*,R^*) occurs via the carbonyl de-coordination/coordination step resulting in

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http://dx.doi.org/10.1016/j.ica.2015.04.029
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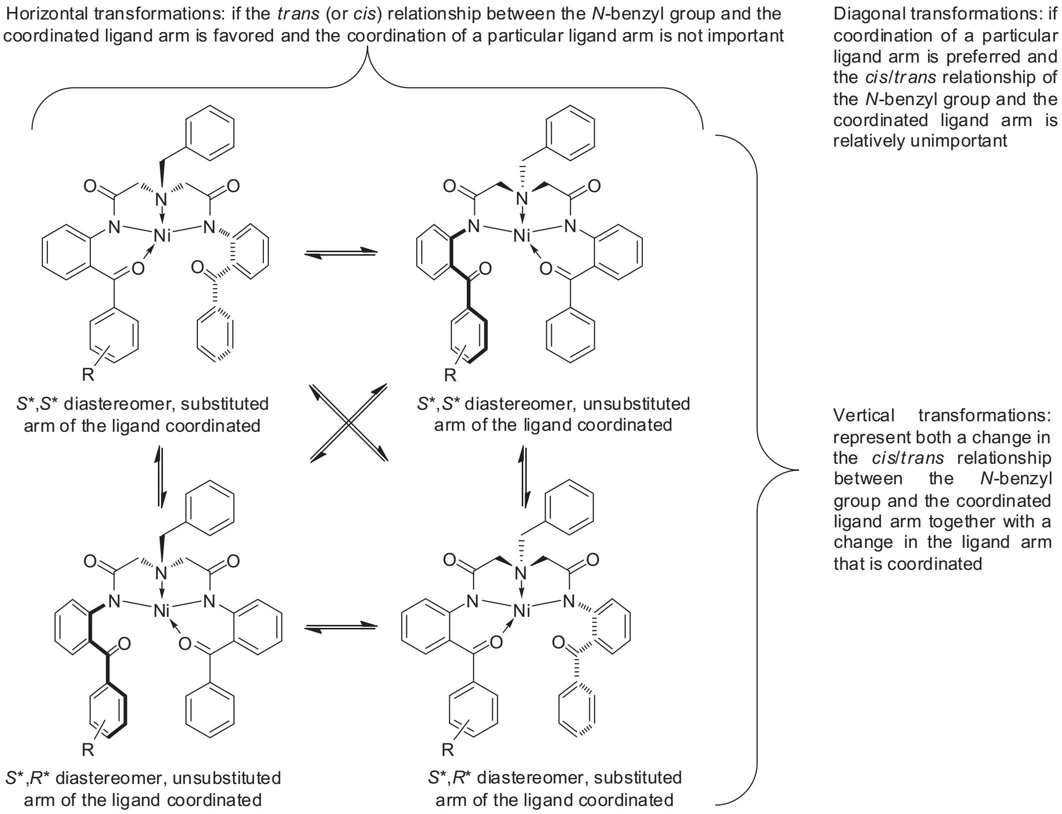

Scheme 1. Formation of diastereomerically switchable complexes from chiral ligands.

inversion of the stereogenic center chirality whilst retaining the same sense of the axial chirality, i.e. the vertical transitions in Scheme 1.[1] If retention of the *cis*/*trans* relationship of the *N*-benzyl group and the coordinated ligand arm is favored but the coordinating sidearm is not, then the horizontal transformations are in operation while conversely if the *cis*/*trans* relationship of the *N*-benzyl group and the coordinated ligand arm is unimportant but the coordinating sidearm is, then the diagonal transformations are in effect. Importantly, it should be noted that due to the structural rigidity of the complexes, a process such as the vertical transition can occur with near complete (>99%) stereoselectivity.

Previously, to evolve the molecular system with differently substituted sidearms in terms of predictability, we introduced electron-withdrawing or -donating substituents to influence the preference for coordination of the *N*-(*o*-benzophenone) amide carbonyls [5]. While the reported data were quite convincing, we felt that only two examples for the Ni^{II} and one for the Pd^{II} complexes were insufficient to consider this approach for controlling the coordination preferences completely explored and proven. Therefore, we decided to extend our study to the synthesis of an additional series of fluorinated and non-fluorinated Ni^{II} and Pd^{II} complexes to further understand the processes and factors involved in the system interconversion, the preferential binding modes, as well as peculiarities of the crystallographic packing. Characterization of the complexes was enabled in the solid state by X-ray crystallographic analysis supported by NMR and MS measurements. The relative energies of the structures with respect to configuration and coordination site were evaluated by DFT calculations to further complement and comprehend the results.

2. Results and discussion

Continuing our modular approach for the design and synthesis of pentadentate ligands and the consequent metal complexes [7], we prepared ligands **5a**–**c** in high yields, starting from the acetyl-protected 2-aminobenzophenones **1a**–**c**, readily available by aryl Grignard additions to 2-methyl-4*H*-3,1-benzoxazin-4-one (Scheme 2). **1a**–**c** were first hydrolyzed to the free 2-aminobenzophenones **2a**–**c**, and then converted to amides **3a**–**c** by treatment with bromoacetyl bromide. These compounds encompassed electron-donating *ortho*-methyl, –*o*-Me, (**3a**) and *para*-methoxy, –*p*-OMe, (**3c**) groups as well as an electron-withdrawing *para*-trifluoromethyl, –*p*-CF_3, (**3b**) group. Compounds **3a**–**c** were transformed to pentadentate ligands **5a**–**c** by reaction with the ring-unsubstituted benzlyamine moiety **4** [7c], also in high yields. Treatment of **3c** (Scheme 3) with benzylamine yielded intermediate **7** [5,8], which upon reaction with **3b** yielded pentadentate ligand **8** functionalized on both sidearms, again in high yield.

The synthesis of Ni^{II} and Pd^{II} complexes **6a**–**e** (Schemes 2 and 3) proceeded straightforwardly by the reaction of $Ni(NO_3)_2{\cdot}6H_2O$ (**6b**,**d**,**e**) or $PdCl_2$ (**6a**,**c**) together with the appropriate ligand (**5a**–**c** or **8**) in methanol under basic conditions [7c,9], though with only modest (Ni complexes) or poor (Pd complexes) yields being obtained.

Crystals of complexes **6a**–**e** amenable for X-ray analysis were obtained in each case by slow evaporation from either CH_2Cl_2 (**6b**–**e**) or EtOAc (**6a**) solutions overlaid with *n*-hexane. This usually required great perseverance and was very demanding and only very small crystals could be obtained in some cases. The details of X-ray crystallographic data collection and refinement for Ni^{II} and Pd^{II} complexes **6a**–**e** are summarized in Table 1.

Previously we have examined CF_3-containing Ni^{II} and Pd^{II} complexes **6f**–**h** (Fig. 1) and found full consistency between the

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[1] The assignment of configuration at the stereogenic center, the N atom, follows the convention outlined previously (Ref. [5]) in that covalent bonds are not considered to take undue preference over coordinating bonds.