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# Water-soluble NNN-pincer complexes of cobalt, nickel and palladium: Solid-state structures and catalytic activity

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Abstract. Neutral NNN-pincer ligand 1 based on a pyridyl core and cyclic amidine pendant arms was synthesized via a straightforward condensation reaction. Its square-planar palladium acetate complex 2 was prepared in methanol and featured a cyclic, hexameric solid-state structure assembled through moderately strong N $\cdots$ H $\cdots$ O hydrogen bonds involving the ligand backbone and the non-coordinated acetate group. The octahedral, diamagnetic Co(III) complex 3 was prepared via in-situ air oxidation of its Co(II) analog. Its solid-state structure confirmed the oxidation state of the metal and revealed the presence of weak bridging and terminal N-H $\cdots$ Cl hydrogen bonds. Paramagnetic nickel complex 4 was prepared in a similar fashion to 1 and was postulated to have a covalent attachment of the acetate moieties to the metal. Derivatives 2 and 3 had excellent water solubility and stability while 4 was sparingly soluble in water. Cyclic voltammetry revealed electrochemically reversible electron transfer steps corresponding to the Co(II)/Co(III) and Ni(II)/Ni(III) redox couples at -0.31 V and 1.04 V vs. SHE, respectively. Complex 4 displayed catalytic competency towards the thiolation of iodobenzene with dimethyldisulfide and zinc in DMF. In water, 4 was able to catalyze the Negishi cross-coupling of iodobenzene.

### 1. Introduction

Following the remarkable success of 2,2':6',6"-terpyridine ligands **I** (terpy or tpy) in coordination chemistry and catalysis (Chart 1),<sup>1,2,3,4</sup> other symmetric, neutral NNN-pincer ligands with pyridine central moieties and unsaturated nitrogen pendant donors have been pursued. An obvious further development was the replacement of the pyridine side arms with other aromatic six-membered nitrogen heterocycles such as pyrazine (**II**),<sup>5,6</sup> pyrimidine (**III**),<sup>5,7</sup> 1,3,5- and 1,2,4-triazine (**IV**<sup>8</sup> and **V**,<sup>9,10,11</sup> respectively) and 1,2,4,5-tetrazine (**VI**).<sup>12,13,14,15</sup> Ligand scaffolds having five-membered nitrogen heterocycles such as imidazole (**VII**),<sup>16</sup> pyrazole (**VIII**),<sup>17,18,19,20,21</sup> as well as 1,2,4- and 1,2,3-triazole (**IX**,<sup>22</sup> **X**,<sup>23</sup> and **XI**,<sup>24,25</sup> respectively) as pendant arms have been employed extensively, with **VIII** proving to be a particularly popular choice.<sup>26</sup> Ligands **XII**,<sup>27</sup> **XIII**,<sup>28</sup> and **XV**<sup>29</sup> featuring oxazolyl, thiazolyl and thiazolinyl pendant

arms, respectively, have been reported as well, although their applications are dwarfed by those of their oxazolinyl analogs **XIV** (PyBOX).<sup>30,31,32,33</sup> 1-pyrroline (**XVI**),<sup>34</sup> 2-imidazoline (**XVII**),<sup>35,36</sup> and 5,6-dihydro-4H-1,3-oxazine (**XIX**)<sup>37</sup> have also been incorporated in pyridyl-based NNN-pincer ligands, while the chemistry of ligands **XVIII** with acyclic imine pendant arms has been explored extensively.<sup>38</sup>



Chart 1. Selected symmetric, neutral NNN-pincer ligands with pyridine central moieties and unsaturated nitrogen pendant donors.

Complexes incorporating the basic ligand frameworks shown in Chart 1 benefit from good ligand properties, easy access via modular synthesis, and superior oxidative stability, and they have been used extensively in homogeneous catalysis,<sup>39,40,41</sup> including olefin polymerization,<sup>42</sup> transfer hydrogenation and enantioselective hydrosilylation.<sup>31</sup> Continuing our investigations into the chemistry of pincer ligands,<sup>43,44</sup> we identified scaffold **XX** as potential candidates for in or on water homogeneous catalysis. Ligand **1** was deemed accessible via one straightforward synthetic step from commercially available starting materials, and its complexes were expected to be soluble in both water and organic solvents. The presence of nitrogen atoms capable to both accept and donate protons in the ligand framework of **1** was expected to enhance the water solubility of its complexes, to provide opportunities for ligand-assisted reactivity,<sup>45,46,47,48,49</sup> and to offer the possibility for variable coordination modes as a neutral (diiminopyridine), mono-(amidoiminopyridine) and dianionic ligand (diamidopyridine). In and on water homogeneous

catalysis has been widely employed in laboratory and industrial scale organic chemistry, owing to improved safety and environmental aspects, decreased cost, ease in separating the catalyst from reaction products, and enhanced reaction rates.<sup>50,51,52,53,54</sup>

#### 2. Results and Discussion



Scheme 1. Synthesis of ligand 1.

The synthesis of the NNN-pincer ligand **1** was carried out via a simple condensation reaction, following the modification of a procedure reported for an anionic phenylene analog (Scheme 1).<sup>55</sup> The crude product was obtained by refluxing dipicolinic acid and 2,2-dimethylpropane-1,3-diamine in ethylene glycol, using *p*-toluenesulfonic acid as a catalyst. The neutral diamine was used instead of the reported hydrochloride acid salt, in order to simplify the synthesis. The crude product precipitated upon cooling and was collected, washed, dried and subsequently used without further purification for the synthesis of metal complexes.



Scheme 2. Synthesis of Pd(II) complex 2.

The palladium acetate complex, **2**, was obtained by refluxing the ligand with the corresponding metal salt in methanol overnight (Scheme 2). Removing the solvent in vacuo left behind the crude product as a yellow solid that was washed with small quantities of acetone and dried. Complex **2** was well soluble in protic solvents such as water and methanol, with no noticeable degradation of the solutions upon exposure to air over one month. The <sup>1</sup>H NMR spectrum was recorded in D<sub>2</sub>O and featured two resonances in a 1 : 1 ratio at 3.00 and 3.24 ppm, corresponding to the two methylene groups rendered inequivalent upon coordination. As expected for a  $C_s$  symmetric product, only one signal was observed for the methyl groups of the pincer ligand, at 1.07 ppm. The broad resonances corresponding to the inequivalent acetate groups at 2.12 and

1.96 ppm suggest an exchange between free and bound acetate in solution. The signals corresponding to the acetate groups were barely visible in the <sup>13</sup>C NMR spectrum, indicating that coalescence occurred very close to room temperature.



Fig. 1. Supramolecular association of 2 in the solid state via  $N-H\cdots O$  hydrogen bonds. Left, balland-stick model with all hydrogen atoms that are not involved in hydrogen bonding removed for clarity. Right, space filling model including all atoms.

Single crystals suitable for X-ray crystallography were grown at room temperature over a period of two weeks from a concentrated solution of **2** in dimethylsufoxide. The solid-state structure revealed the formation of cyclic, hexameric associates with  $D_{3d}$  symmetry, described as formally featuring cationic palladium pincer complexes [(1)PdOAc]<sup>+</sup> connected by the acetate counterions (Figure 1). These non-coordinated acetate groups form moderately strong N····H···O hydrogen bonds (N2···O distance 2.717(5) Å) with the pendant amines in the pincer ligand framework. The supramolecular associates have an internal diameter of *ca*. 20 Å and an external diameter of *ca*. 30 Å; however, due to packing this does not translate into voids in the crystal structure. The expected NNN-pincer coordination with one bonded acetate group is observed in the [(1)PdOAc]<sup>+</sup> ions, generating a distorted square-planar geometry at the metal (Figure 2). The N1-Pd1-N1' angle of 161.24(9)° is slightly wider than in NNN-palladium pincer complexes with imine side arms (155-160°), and much more typical of 2,2':6',6"-terpyridine complexes (*e.g.* 162.0(1)° in [Pd(terpy)(OH)]<sup>+</sup>).<sup>56</sup> Both pendant rings adopt a half-chair conformation in the solid state, displaying a cisoid arrangement with respect to the palladium-coordinated acetate moiety. The N1-C6 and N2-C6 bonds are very similar in length (1.312(3) and 1.330(3) Å, respectively),

indicating extensive electron delocalization, as outlined in Scheme 2. Typical of NNN pincer architectures, the central Pd-N bond is 0.1 Å shorter than the Pd-N bonds involving the pendant arms. This reflects geometric constrains, rather than electronic effects, as illustrated by the structure of  $[(terpy)PdPy](ClO_4)_2$ .<sup>57</sup>



**Fig. 2.** Solid state structure of the cation in **2** with thermal ellipsoids drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): Pd1-N1 = 2.0237(18), Pd1-N3 = 1.922(2), Pd1-O1 = 2.015(2), N3-C7 = 1.338(2), N1-C6 = 1.312(3); N2-C6 = 1.330(3), C6-C7 = 1.484(3); N1-Pd1-N1' = 161.24(9), N3-Pd1-O1 = 176.35(10), C7-N3-C7' = 123.7(2), N1-C6-N2 = 125.01(19), N1-C6-C7 = 115.64(18)

Complex **3** was synthesized by refluxing two equivalents of **1** with cobalt (II) chloride hexahydrate in air overnight (Scheme 3). The dark precipitate was filtered off and the solvent was removed in vacuo, leaving behind the product as a dark yellow-green solid. Under exclusion of air, the reaction failed to produce the desired compound, confirming that atmospheric oxygen was responsible for the oxidation of Co(II) to Co(III). The oxidation of Co(II) to Co(III) in complexes with nitrogen-based ligands with either air or hydrogen peroxide has been described.<sup>58</sup> Diamagnetic complex **3**, having a low spin d<sup>6</sup> electronic configuration, is soluble and stable in protic solvents (*i.e.* water and methanol) and was characterized by NMR using D<sub>2</sub>O as a solvent. Resonances corresponding to the chemically inequivalent methylene groups were observed at 1.97 and 3.17 ppm in the <sup>1</sup>H NMR spectrum. Only one resonance was observed at 0.81 ppm for all methyl groups of the ligand, as expected for time-averaged  $D_{2d}$  symmetry.



Scheme 3. Synthesis of Co(III) complex 3.

Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of **3** in a methanol-toluene mixture. The solid-state structure revealed that the trication  $[(1)_2\text{Co}]^{3+}$  crystallized with three chloride anions, instead of the stoichiometric product featuring two chloride ions and one hydroxide (Figure 3). The presence of a small proportion of disordered hydroxide ions on the site of the chlorides can however not be excluded. Two of the chloride ions are weakly hydrogen bonded to the cation (Cl1…N2 = 3.177(4) Å) while the third bridges the cations via weak hydrogen bonds, forming a linear supramolecular arrangement (Cl2…N4 = 3.208(4) Å).



**Figure 3.** Fragment from the solid-state structure of pseudo-octahedral complex **3** in a combination of thermal ellipsoids drawn at 50% probability level and wireframe. All hydrogen atoms that are not involved in hydrogen bonding have been removed for clarity. Selected bond lengths (Å) and angles (deg): Co1-N3 = 1.861(2), Co1-N1 = 1.936(2), Co1-N5 = 1.937(2), N3-C7 = 1.330(4), N3-C11 = 1.343(4), N1-C6 = 1.312(4), N2-C6 = 1.331(4), N5-C12 = 1.311(4), N4-C12 = 1.330(4); N1-Co1-N5 = 163.68(9), N3-Co1-N3' = 178.96(15).



Figure 4. Cyclic voltammogram 3 (top) and 4 (bottom) (1 mmol solution in water with 0.1 M  $Na_2SO_4$  as supporting electrolyte, 3 mm diameter glassy carbon working electrode, scan rate 0.025 (3) and 0.05 Vs<sup>-1</sup> (4), Ag/AgCl reference electrode).

The structure of the cation is unremarkable, with a pseudo-octahedral geometry at the metal (N1-Co1-N5 =  $163.68(9)^{\circ}$ , N3-Co1-N3' =  $178.96(15)^{\circ}$ ) and shorter Co-N bonds involving the pyridyl nitrogen, N3, than those with the amidine nitrogens, N1 and N5. Cyclic voltammetry showed an electrochemically-reversible reduction attributed to the Co(II)/Co(III) redox couple at -0.31 V *vs*. SHE (Figure 4). This value is similar to those observed for comparable octahedral cobalt complexes with nitrogen ligands, which fall between 0.1 and -0.6 V.<sup>59</sup>

Nickel acetate complex 4 was synthesized through a synthetic route similar to the one used for the palladium and cobalt complexes, by simple coordination of **1** to hydrated nickel acetate in methanol (Scheme 4). The resulting dark solution was evaporated to dryness in vacuo, and the remaining dark red-brown solid was collected and used without further purification. The paramagnetic nickel complex is soluble in alcohols, especially methanol, and air stable, but only moderately soluble in water. A high-resolution ESI-MS spectrum showed a signal corresponding to the m/z ratio and isotopic distribution of the  $[(1)Ni(OAc)]^+$  ion. Based on this and its paramagnetic nature, we proposed the structure  $[(1)Ni(OAc)_2]$  for 4, as shown in Scheme 4, which has been proven by means of X-ray crystallograpy for [(terpy)Ni(OCOtBu)<sub>2</sub>].<sup>60</sup> Solution equilibria involving species such as  $[(1)Ni(OAc)]^+(OAc)^-$ ,  $\{[(1)Ni(OAc)]_2(\mu - OAc)_2\}^+$  and  $[(1)_2Ni]^{2+2}(OAc)^{-1}$  are possible but the limited solubility of 4 in water in comparison to 2 and 3 supports a monomeric or dimeric molecular structure with both acetate groups covalently bonded to the metal, over an ionic structure. Cyclic voltammetry showed one electrochemicallyreversible electron transfer within the solvent window of water at 1.04 V vs. SHE, corresponding to the Ni(II)/Ni(III) redox couple (Figure 3). No reduction to metallic nickel, which is characteristic of nickel acetate, was observed,<sup>61</sup> and no attempts have been made to isolate the oxidized Ni(III) species via chemical or electrochemical means.



Scheme 4. Synthesis of Ni(II) complex 4

NNN- and PCP-Ni pincer complexes have been shown to selectively catalyze the thiolation of aryl halides in a one-pot reaction involving disulfides and elemental zinc as a reducing agent.<sup>62,63,64</sup> A preliminary assessment of **4** using a 5 mol % catalyst loading in DMF and reaction monitoring by GC-MS showed the expected cross-coupled product in low yields (Scheme 5). A control experiment using hydrated nickel acetate was also performed under similar conditions with limited success (Table 1). Using water as a solvent, a preference for the formation of biphenyl via Negishi coupling instead of carbon-chalcogen coupling was observed. This line of investigation was pursued with a 2.5 mol % catalyst loading, leading to turnover

numbers of 10 towards the coupled product (Scheme 6). No catalytic activity was observed in a control experiment using 5 mol % nickel acetate hydrate under similar conditions. Both Ni(0)<sup>65</sup> and Ni(I)<sup>63</sup> intermediates have been postulated for similar transformations in organic solvents. Proficient palladium-based catalysts for the Negishi coupling in water in the presence of polyoxyethanyl  $\alpha$ -tocopheryl sebacate as surfactant have been reported,<sup>66,67,68</sup> but to our knowledge this is the first report of nickel-catalyzed Negishi coupling in water. Preliminary experiments using **2** showed that this catalyzed the Negishi cross-coupling in water, but also the subsequent partial hydrogenation of the resulting biphenyl.



Scheme 5. Thiolation of iodobenzene in the presence of 4.



Scheme 6. Negishi coupling in the presence of 4.

Reaction	Catalyst	Catalyst loading (mol %)	Product yield $(\%)^a$
Thiolation	4	5	24
Thiolation	Ni(OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub>	6	8
Negishi	4	2.5	28
Negishi	$Ni(OAc)_2(H_2O)_4$	4.5	0

Table 1: Exploratory catalysis with complex 4 compared to Ni(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>

<sup>a</sup> Yields were determined by GC-MS relative to iodobenzene

### 3. Conclusions

Neutral pincer ligand 1 was accessed via a facile condensation reaction starting from commercially available starting materials. Its metal complexes were obtained by heating the ligand with the appropriate metal salt in methanol. The water soluble, square-planar palladium acetate NNN-pincer complex 2 was characterized by NMR, ESI-MS, and elemental analysis. X-ray crystallography revealed a cyclic, hexameric structure in the solid state, with the non-

coordinated acetate group bridging the cationic metal complexes. Diamagnetic cobalt complex **3** was obtained via in-situ oxidation of its in-situ obtained Co(II) analog with atmospheric oxygen and was characterized by NMR, ESI-MS and cyclic voltammetry. X-ray crystallography revealed an octahedral, homoleptic metal complex with three non-coordinated chlorides engaged in weak hydrogen bonding with the cationic cobalt complex. Paramagnetic Ni(II) NNN-pincer complex **4** was characterized by ESI-MS and cyclic voltammetry, and its catalytic application toward thiolation and Negishi coupling were investigated on an exploratory basis. As postulated, ligand **1** proved to be able to form stable metal complexes that were soluble in both water and organic solvents. Aside from enhancing the solubility of the complexes in protic solvents, hydrogen bonding involving the protons on the ligand backbone was responsible for forming supramolecular associates in the solid state. Nickel complex **4** displayed catalytic activity towards the reductive thiolation of iodobenzene with dimethyldisulfide in DMF in the presence of zinc. More significantly, **4** is to our knowledge the first example of a nickel catalyst that promotes the Negishi coupling in water. Further studies towards in- and on-water catalysis pertaining to complexes **2** and **4** are in progress.

### 4. Associated Content:

Supporting Information: Complete NMR spectra for all new diamagnetic compounds, GC-MS spectra as well as the relevant crystallography tables and cif files are provided in the Supporting Information. CCDC 1565556 and 1565557 contains the supplementary crystallographic data for 2 3. free and These data can be obtained of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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#### 7. Experimental

**General Considerations** 

All reagents were purchased from chemical suppliers and used as received. Unless specified otherwise, the synthesis and handling of compounds was carried out without rigorous exclusion of air and moisture. <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on a Bruker Avance 400 spectrometer and internally referenced relative to  $D_2O$  (<sup>1</sup>H, 4.79 ppm) or deuterated methanol (<sup>1</sup>H, 3.31 ppm; <sup>13</sup>C, 49.15 ppm). The <sup>13</sup>C NMR spectra recorded in D<sub>2</sub>O were calibrated using CH<sub>3</sub>CN as an internal standard ( $^{13}$ C, 1.47 ppm). Coupling constants (J) are reported as absolute values. Combustion analyses were performed on a Perkin Elmer 2400 Series II CHNS Analyzer. All chromatograms were collected on an Agilent model 5975 GC-MSD using a method with injection temperature of 250 °C, initial temperature of 50 °C, in increments of 10 °C per minute. ESI-MS was performed with an Agilent 6520 ESI QTOF instrument. Samples were injected in MeOH solution with a flow rate of 0.2 mL per minute, the source was held at 200 °C, the drying gas has a pressure of 12 psi and a flow rate of 7 L /minute, and the fragmentor voltage was set to 80V. Cyclic voltammetry was performed using a PARSTAT 2273 potentiostat, a glassy carbon working electrode (d = 3 mm), a saturated Ag/AgCl reference electrode and a platinum counterelectrode. X-ray crystallographic analyses were performed on suitable single crystals coated in Paratone oil and mounted on a glass fiber. Measurements were collected on either a Nonius KappaCCD or a Bruker APEX II CCD diffractometer; full details can be found in the independently deposited crystallography information file (cif).

### 7.1. Synthesis of 2,6-bis(5,5-dimethyl-tetrahydropyrimidine)pyridine 1

Pyridine-2,6-dicarboxylic acid (4.820 g, 28.8 mmol), 2,2-dimethylpropane diamine (8.00 mL, 66.6 mmol) and *p*-toluenesulfonic acid (0.445 g, 2.3 mmol) were placed in a 100 mL round bottom flask equipped with magnetic stirrer and refluxed overnight in 50 mL of ethylene glycol. After cooling the resulting solution in an ice bath, the white solid that precipitated was collected by filtration and washed with water (20 mL) in an ultrasonic bath in order to remove residual glycol. The suspension was filtered and washed with acetone to afford **1** (4.012 g, 47% yield) as a white powder. <sup>1</sup>H NMR (400 MHz, methanol- $d_4$ ):  $\delta$  1.00 (s, 12 H,  $CH_3$ ), 3.14 (s, 8 H,  $CH_2$ ), 7.92 (t, 1H, J = 7.9 Hz, p-CH), 8.11 (d, J = 7.9 Hz, 2 H, m-CH). <sup>13</sup>C NMR (101 MHz, methanol-

*d*<sub>4</sub>) δ 25.3 (CH<sub>3</sub>), 27.0 (*C*(CH<sub>3</sub>)<sub>2</sub>), 54.6 (CH<sub>2</sub>), 122.8 (*m*-CH), 138.9 (*p*-CH), 151.2 (*o*-CH), 153.7 (CN<sub>2</sub>).

#### 7.2. Synthesis of Pd(II) complex 2

Ligand **1** (100 mg, 0.33 mmol) and anhydrous palladium (II) acetate (74 mg, 0.33 mmol) were stirred overnight at 60 °C in methanol (15 mL). The solvent was subsequently removed in vacuo and the yellow-orange solid residue was washed with small quantities of acetone, yielding 110mg of complex (64% yield). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  1.07 (s, 12 H, CH<sub>3</sub>), 1.96 (s, 3 H, CH<sub>3</sub>COO), 2.12 (s, 3 H, CH<sub>3</sub>COO), 3.00 (s, 4 H, CH<sub>2</sub>), 3.24 (s, 4 H, CH<sub>2</sub>), 7.98 (d, *J* = 8.2 Hz, 2 H, *m*-CH), 8.43 (t, 1H, *J* = 8.2 Hz, *p*-CH). <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O)  $\delta$  24.0 (CH<sub>3</sub>), 27.0 (*C*(CH<sub>3</sub>)<sub>2</sub>), 50.1 (CH<sub>2</sub>), 57.7 (CH<sub>2</sub>), 124.3 (*m*-CH), 142.5 (*p*-CH), 152.3 (*o*-CH), 159.3 (CN<sub>2</sub>). Elemental analysis (%): Calcd for C<sub>21</sub>H<sub>31</sub>N<sub>5</sub>O<sub>4</sub>Pd: C 48.14, H 5.96, N 13.37; Found: C 46.95, H 6.07, N 12.99. HRMS (ESI): m/z calcd for C<sub>19</sub>H<sub>28</sub>N<sub>5</sub>O<sub>2</sub>Pd, [(1)PdOAc]<sup>+</sup>: 464.1278, found: 464.1280.

#### 7.3. Synthesis of Co(III) complex 3

Ligand **1** (450 mg, 1.51 mmol) and cobalt (II) chloride hexahydrate (180 mg, 0.75 mmol) were refluxed overnight in methanol (15 mL) in air. The black precipitate was subsequently filtered off and the solution was evaporated to dryness in vacuo. The product was isolated as a yellow-green solid. (402mg, 73% yield). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  0.81 (s, 12 H, CH<sub>3</sub>), 1.97 (s, 4 H, CH<sub>2</sub>), 3.17 (s, 4 H, CH<sub>2</sub>), 8.52 (d, *J* = 7.9 Hz, 2 H, *m*-CH), 8.79 (t, 1H, *J* = 8.1 Hz, *p*-CH). <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O)  $\delta$  24.2 (CH<sub>3</sub>), 27.8 (*C*(CH<sub>3</sub>)<sub>2</sub>), 49.9 (CH<sub>2</sub>), 54.3 (CH<sub>2</sub>), 126.0 (*m*-CH), 143.8 (*p*-CH), 153.7 (*o*-CH), 157.2 (CN<sub>2</sub>). HRMS (ESI): m/z calcd for C<sub>34</sub>H<sub>49</sub>N<sub>10</sub>CoCl, [(**1**)<sub>2</sub>CoCl<sup>2+</sup> - H<sup>+</sup>]<sup>+</sup>: 691.3162, found: 691.3138.

### 7.4. Synthesis of Ni(II) complex 4

Ligand **1** (204 mg, 0.68 mmol) and nickel (II) acetate tetrahydrate (166 mg, 0.67 mmol) were stirred overnight at 60 °C in methanol (25 mL). The solvent was subsequently removed in vacuo and the product was isolated as a red-brown solid (253 mg, 78% yield). HRMS (ESI): m/z calcd for  $C_{19}H_{28}N_5O_2Ni$ ,  $[(1)NiOAc]^+$ : 416.1597, found: 416.1585.

### 7.5. Thiolation of iodobenzene in the presence of 4

Iodobenzene (34  $\mu$ L, 0.3 mmol), zinc powder (20 mg, 0.3 mmol), dimethyldisulfide (13 $\mu$ L, 0.15 mmol) and **4** (7 mg, 0.015 mmol) were heated in DMF at 110 °C overnight A small portion of the mother liquor was diluted in chloroform and analyzed by GC-MS. The peak at 8.7 min. correlated to iodobenzene and the peak 14.1 minutes corresponded to thioanisole.

### 7.6. Thiolation of iodobenzene in the presence of $Ni(OAc)_2(H_2O)_4$

Iodobenzene (34  $\mu$ L, 0.3 mmol), zinc powder (20 mg, 0.3 mmol), dimethyldisulfide (13  $\mu$ L, 0.15 mmol) and nickel acetate tetrahydrate (5 mg, 0.02 mmol) were heated in DMF at 110 °C overnight. A small portion of the mother liquor was diluted in chloroform and analyzed by GC-MS. The peak at 8.7 min. correlated to iodobenzene and the peak 14.1 min. corresponded to thioanisole.

### 7.7. Negishi coupling in the presence of 4

Iodobenzene (51  $\mu$ L, 0.45 mmol), zinc powder (30 mg, 0.46 mmol) and 4 (5 mg, 0.01 mmol) were heated in water at 100 °C overnight. A chloroform extract of the sample was diluted and analyzed by GC-MS. The peak at 8.7 minutes correlated to iodobenzene and the peak 14.1 minutes corresponded to biphenyl.

### 7.8. Negishi coupling in the presence of $Ni(OAc)_2(H_2O)_4$

Iodobenzene (51  $\mu$ L, 0.45 mmol), zinc powder (30 mg, 0.46 mmol) and Ni(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> (5 mg, 0.02 mmol) were heated in water at 100 °C overnight. A chloroform extract of the sample was diluted and analyzed by GC-MS. The peak at 8.7 minutes corresponded to iodobenzene.

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Palladium, cobalt and nickel complex of a neutral NNN-pincer ligand based on a pyridyl core and cyclic amidine pendant arms were prepared. The palladium and cobalt complexes formed hydrogen-bonded supramolecular associations in the solid state, while the nickel analog displayed catalytic activity towards the Negishi coupling of iodobenzene in water. Acction