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Nickel(II) Schiff base complexes: Synthesis, characterization and catalytic activity in Kumada–Corriu cross-coupling reactions

Vladimír Kuchtanin [a,*], Lucia Kleščíková [b], Michal Šoral [c], Róbert Fischer [b], Zdeňka Růžičková [d], Erik Rakovský [e], Ján Moncol' [a], Peter Segl'a [a]

[a] Institute of Inorganic Chemistry, Technology and Materials, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 81237 Bratislava, Slovak Republic
[b] Institute of Organic Chemistry, Catalysis and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 81237 Bratislava, Slovak Republic
[c] Central Laboratories, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37, Slovak Republic
[d] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic
[e] Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, 84215 Bratislava, Slovak Republic

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ABSTRACT

The syntheses of ten new Ni(II) complexes **5a**–**5j** with H_2L tridentate (ONO) Schiff-base ligand (2-((2-oxybenzylidene)amino)phenolate) have been described and fully characterized by means of elemental analysis, FT–IR, electronic, ^1H NMR and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction. In all [Ni(L)B] complexes (where B are imidazole, 4-benzylpyridine, 2-methyl-5-ethylpyridine, 3-hydroxymethylpyridine, 2-methylbenzimidazole, 2,6-dimethylpyridine, 4-methylpyridine, 2-isopropylbenzimidazole, 4-methylpiperidine or triphenylphosphine) the Schiff base completely deprotonates and coordinates to the metal ion as a dianionic tridentate ligand via the donor oxygens and nitrogen atoms. The coordination number of Ni(II) atoms is four with distorted square-planar stereochemistry. This is in a good agreement with the ligand field band position in their electronic spectra, as well as with the X-ray structure analysis for all complexes under study. Six selected complexes are used as catalysts for Kumada–Corriu cross-coupling reactions and exhibit a moderate to good catalytic activity in the synthesis of biaryl derivatives.

1. Introduction

Schiff-bases are a vital class of organic compounds. A large number of metal complexes with a Schiff-base were reported with various methods of in activation of small molecules, in addition to being nano-precursors and with good redox capability. Attention is paid to their potential applications in many areas, viz. optical utilization [1–3], biology [4,5], catalysis [6–8] and corrosion inhibition [9,10], as well as to their thermal, magnetic and electrical properties [11]. Nickel complexes play a prominent role in bioinorganic redox enzyme systems [12,13] and square planar nickel complexes in concert of some other factors can cause the cleavage of plasmid DNA [14].

2. Results and discussion

2.1. Synthesis of the nickel(II)complexes

The synthetic route of nickel complexes is shown in Scheme 1. The organic precursor H_2L **3** was prepared according to the literature by the condensation of salicylaldehyde (**1**) and 2-aminophenol (**2**) in acetonitrile [15]. Subsequently, all complexes **5a**–**5j** were prepared by stirring an acetonitrile solution of Schiff base with methanolic solution of $Ni(OCOCH_3)_2{\cdot}4H_2O$ and with relevant N-donor ligands (pyridine, piperidine, imidazole and benzimidazole derivatives) or triphenylphosphine in 1:1:1 molar ratio for 2 h under reflux. The resulting red solutions were left to evaporate slowly at ambient temperature. Complexation products were isolated as red-brown (**5a**) or red (**5b**, **5d**–**5j**) crystals and a red (**5c**) powder in good yields (70–80%). The analytical data for these complexes are in good agreement with the proposed molecular formula.

* Corresponding author. Tel.: +421 2593 25 209; fax: +421 2524 93 198.
E-mail address: vladimir.kuchtanin@stuba.sk (V. Kuchtanin).

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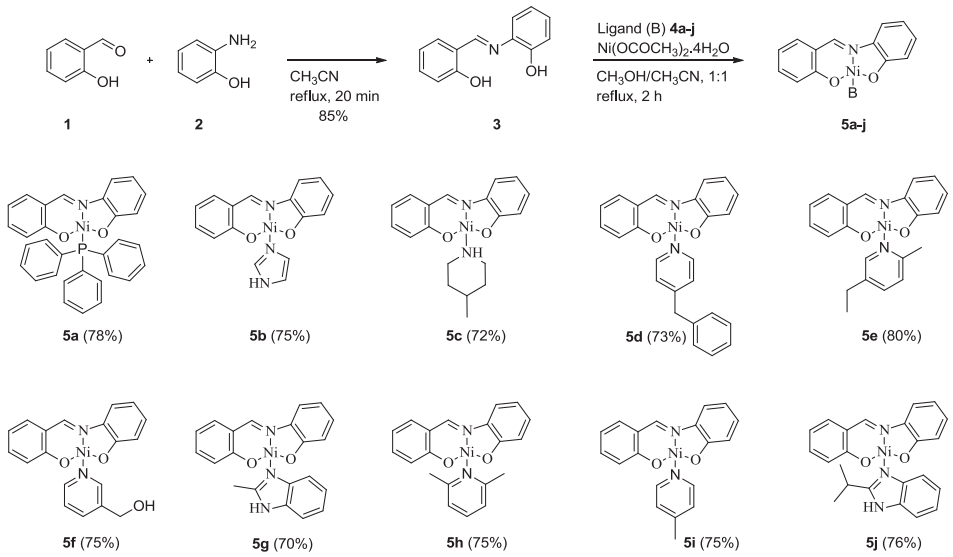


Scheme 1. Synthesis of the nickel(II) complexes.

2.2. Characterization of the complexes

2.2.1. Infrared spectra

The ν(C=N) band at 1625 cm^{-1} of the Schiff base shifts to lower frequencies in complexes indicating weakening of the azomethine band due to the coordination to the metal [16]. The ν(C—O) band for all complexes appears at lower frequencies compared to that for the free ligand, which is due to the participation of phenolic oxygen on chelation [17].

2.2.2. ^{1}H and ^{13}C NMR spectra

The NMR analysis of compounds **5a**–**j** suggested a partial or dominant paramagnetic behavior of the central atom. A considerable line broadening was present in the ^{1}H and ^{13}C NMR spectra of **5d** and **5i**. A dependence of the decrease of T2* relaxation time upon the distance from Ni(II) was observable, resulting in the impossibility to assign (or even observe) some of the ^{13}C signals from the heterocyclic ligands. The NMR measurements of **5f**, **5g** and **5j** resulted in signals which were too broad to attempt a 2D NMR analysis. The rapid T2 relaxation of the signals would cause that the potentially observable signals would relax (and thus disappear) already during the mixing and evolution period of the 2D NMR sequences. High-spin and ligand dependent behavior of Ni(II) complexes was observed in past studies and described in detail [18]. This behavior was noticed when measuring the spectra of **5b** in deuterated chloroform, while measurements of the same substance in deuterated tetrahydrofuran yielded spectra with sharp lines. Based on the above reasons, ^{1}H and ^{13}C NMR spectra for the complexes **5f**, **5g** and **5j** were not recordable, and therefore are not included in Section 4.

2.2.3. Electronic spectra

Ni(II) square-planar complexes typically have a single band at about 22 000 cm^{-1}, and a second more intense band may be seen near 23 000 cm^{-1}. Square complexes under study differ from those with other coordination polyhedra in that the absorption below 10 000 cm^{-1} is not seen [19].

2.2.4. X-ray crystallography

The molecular structures of nine complexes **5a**, **5b**, **5d**–**5j** are drawn in Figs. 1–5 and ESI Figs. S1–S4. The nickel atoms in all compounds have a distorted square planar coordination geometry.

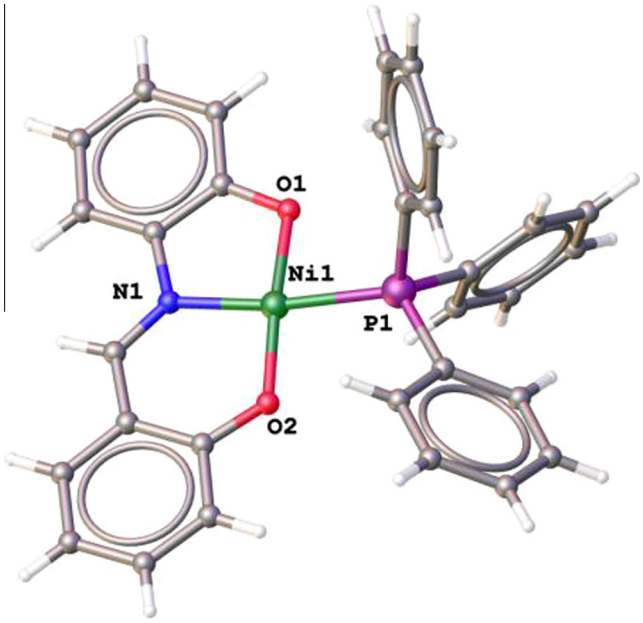


Fig. 1. Molecular structure of complex **5a**. Only one part of disordered ligand is drawn.

Distortion is mainly caused by the presence of the double deprotonated tridentate L ligand (2-((2-oxybenzylidene)amino)phenolate), which forms together with nickel atom one five- and one six-membered metallocycles [O—Ni—N angles are in the ranges 86–88° and 95–98°, respectively]. In all compounds is L bonded to the nickel ion *via* two phenolate oxygen atoms [Ni—O distances are in the range 1.81–1.85 Å, See ESI Table S1] and iminic nitrogen atoms [Ni—N distances are in the range 1.82–1.89 Å, See ESI Table S1]. The crystal structures of two complexes **5b** and **5h** show two crystallographic independent complex molecules (Figs. 2 and ESI S5). The fourth coordination positions are occupied by the phosphorus atom from triphenylphosphine ligand (**5a**) [Ni—P distances are in the range 2.11–2.15 Å, See ESI Table S1] or nitrogen atoms from imidazole (**5b**), 4-benzylpyridine (**5d**), 2-methyl-5-ethylpyridine (**5e**), 3-hydroxymethylpyridine (**5f**), 2-methylbenzimidazole (**5g**), 2,6-dimethylpyridine (**5h**), 4-methylpyridine (**5i**) or 2-isopropylbenzimidazole (**5j**) [Ni—N distances are in the range 1.88–1.95 Å,

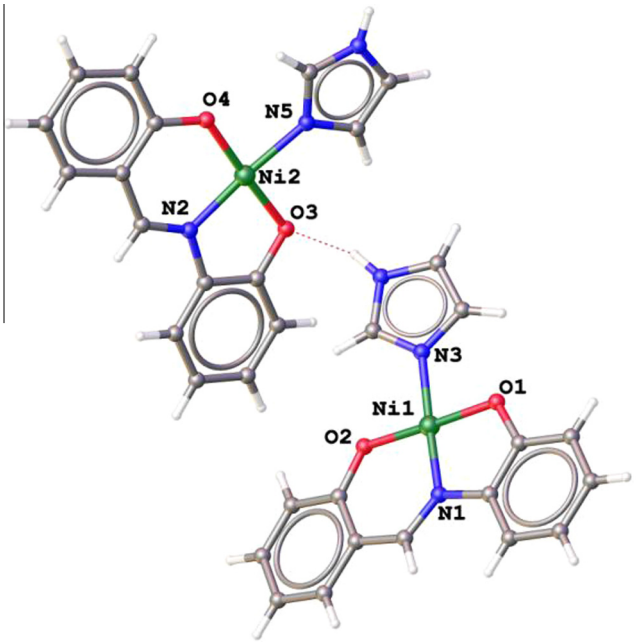


Fig. 2. Molecular structure of complex **5b**.

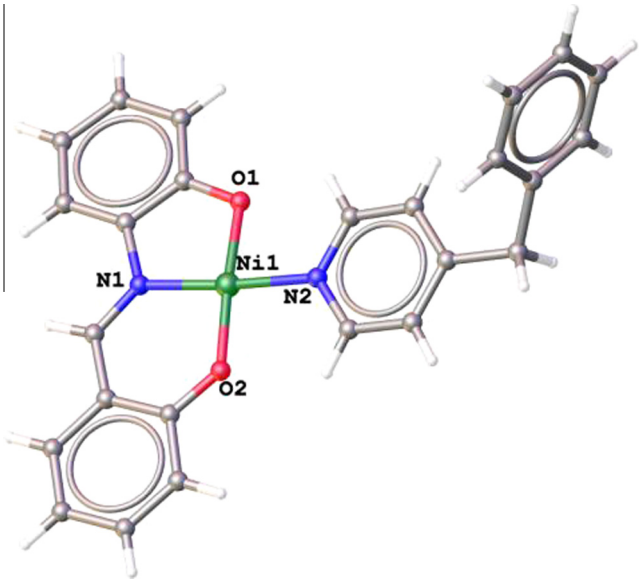


Fig. 3. Molecular structure of complex **5d**. Only one part of disordered complex molecule is drawn.

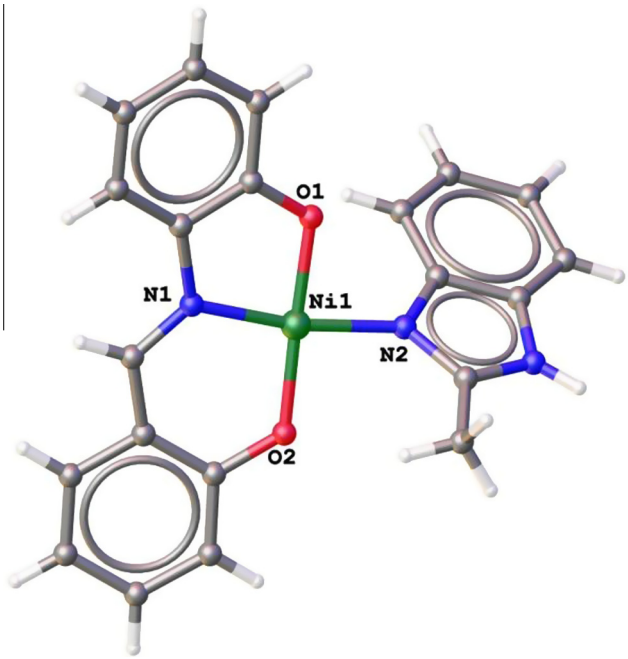


Fig. 4. Molecular structure of complex **5g**. Only one part of disordered ligand is drawn.

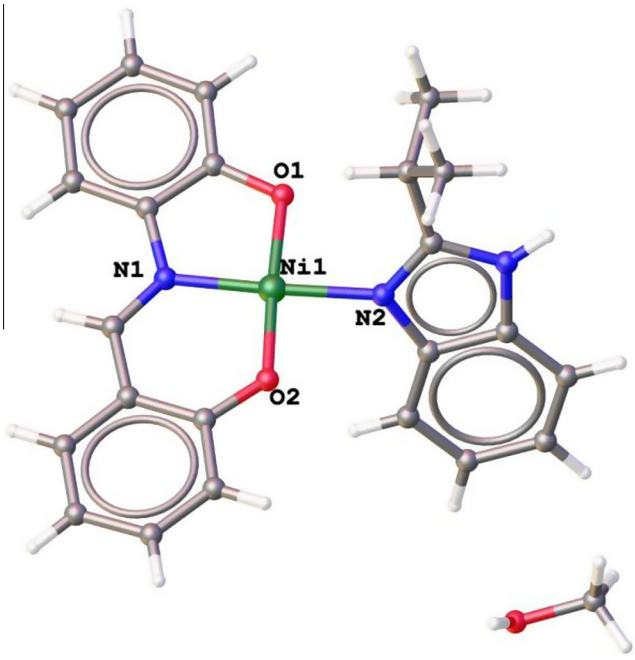


Fig. 5. Molecular structure of complex **5j**. Only one part of disordered ligand is drawn.

See ESI Table S1]. Similar square planar nickel(II) complexes with 1-methylimidazole and triphenylphosphine ligands have been recently published by Salehi et al. [20] and Saha et al. [21].

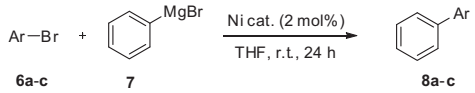
The complex molecules of **5b** are connected through N—H···O hydrogen bonds between imidazole ligand and phenolate oxygen atoms of L_1 [N···O distances are in the range 2.773(5)–2.826(6) Å (See ESI Table S2)], forming supramolecular spiral (See ESI Fig. S5). The two complex molecules of **5f** are joined into supramolecular ring $R_2^2(14)$ [22] (See ESI Fig. S6) through O—H···O hydrogen bonds between hydroxyl groups of 3-hydroxymethylpyridine ligand and phenolate oxygen atoms of L_1 [O···O distance of 2.743(5) Å (See ESI Table S2)]. The complex molecules of **5g** are linked through N—H···O hydrogen bonds between imidazole ring and phenolate oxygen atoms of L_1 [N···O distance of 2.756(5) Å (See ESI Table S2)] into supramolecular *zigzag* chain (See ESI Fig. S7). The crystal structure of **5j** consists of complex molecules and uncoordinated methanol molecules, which are connected into supramolecular ring $R_4^4(16)$ [22] (See ESI Fig. S8) through N—H···O hydrogen bonds between imidazole rings of 2-isopropylbenzimidazole ligand and methanol molecules [N···O distance of 2.802(5) Å (See ESI Table S2)], and O—H···O hydrogen bonds between methanol ligands and phenolate oxygen atoms of L_1 [O···O distance of 2.662(5) Å (See ESI Table S2)]. The similar supramolecular rings have been formed in crystal structure of

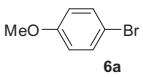
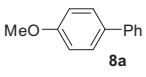
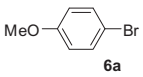
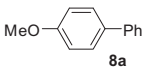
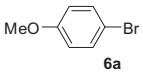
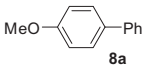
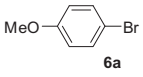
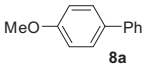
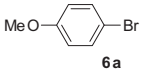
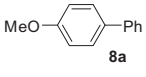
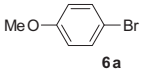
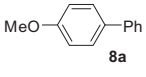
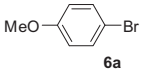
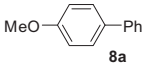
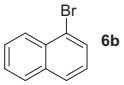
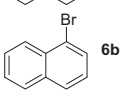
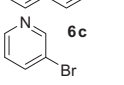
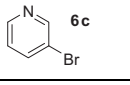
(4-chloro-2-((2-(hydroxy)benzylidene)amino)phenolato)(1H-imidazole)-nickel methanol solvate (refcode: ZUFVUT) [23]. On the other hand, supramolecular *zigzag* chain have been observed in crystal structure of (4-chloro-2-((2-(hydroxy)benzylidene)amino) phenolato)-(2-methyl-1H-imidazole)-nickel methanol solvate (refcode: SUBJEG) [24].

2.3. Catalytic activity of the nickel(II)complexes

The catalytic activity of the selected Ni(II) complexes **5a**–**d**, **5g** and **5j** was readily examined in Kumada–Corriu cross-coupling reaction [25], which is still one of the most attractive method for the synthesis of biphenyl derivatives [26]. 4-Bromoanisole (**6a**) and phenylmagnesium bromide (**7**) were chosen as initial model substrates. All attempts were carried out in a Schlenk tube in the presence of 2 mol% of nickel complexes for 24 h under argon atmosphere (Table 1). Commercially available Ni(dppp)Cl_2 was used as a competitive catalyst. The results summarized in Table 1 show that three of the tested complexes **5a**,**c** and **5d** exhibit good catalytic activity, and the desired product 4-methoxybiphenyl (**8a**) was isolated in 65–70% yields, despite of different ligands used (entries 2, 4 and 5). Moreover, the yields were even higher than that with Ni(dppp)Cl_2 (57%, entry 1). On the other hand, complexes **5b**, **5g** and **5j**, containing the imidazole and the benzimidazole ligands were less active. The presence of hydrogen atom attached to the nitrogen atoms probably governed the catalytic activity of **5b**, **5g** and **5j** due to their facile deprotonation, and 4-methoxybiphenyl (**8a**) was obtained in lower 49% and 42% yields (entries 3, 6 and 7), respectively. Apart from the isolated yields, no homocoupling side-products were detected by inspection of NMR spectra of the crude reaction mixtures. To extend the utilization of the catalysts, two complexes **5a** and **5d**, showing the best activity, were applied in cross-coupling reactions of phenylmagnesium bromide (**7**) with 1-bromonaphthalene (**6b**) and 3-bromopyridine (**6c**). The reactions were performed under same reaction conditions as described above. Results again showed the good catalytic activity of both complexes. The reaction of 1-bromonaphthalene (**6b**) provided desired 1-phenylnaphtalene (**8b**) in very good 81% and 78% isolated yields, respectively (entries 8 and 9), in comparison to the reactions of 3-bromopyridine (**6c**), which afforded 3-phenylpyridine (**8c**) in lower 60% and 62% yields (entries 10 and 11). It is worth noting that complex **5d**, bearing a pyridine ligand, was more stable than **5a** with a triphenylphosphino group. The latter species was gradually decomposed by storage at room temperature for a longer time, resulting in the loss of its activity.

Table 1
Kumada–Corriu cross-coupling reactions with the selected nickel(II) complexes **5a**–**d**, **5g**, **5j**.[a]



Entry	ArBr	Ni cat.	Product	Yield[c] (%)
1	 **6a**	$NiCl_2$ (dppp)[b]	 **8a**	57
2	 **6a**	**5a**	 **8a**	70
3	 **6a**	**5b**	 **8a**	49
4	 **6a**	**5c**	 **8a**	65
5	 **6a**	**5d**	 **8a**	70
6	 **6a**	**5g**	 **8a**	42
7	 **6a**	**5j**	 **8a**	42
8	 **6b**	**5a**	 **8b**	81
9	 **6b**	**5d**	 **8b**	78
10	 **6c**	**5a**	 **8c**	60
11	 **6c**	**5d**	 **8c**	62

[a] Reagents and conditions: ArBr (2 mmol), Ni cat. (2 mol%, 0.04 mmol), PhMgBr (4 mmol, 1 M in THF), THF (2 mL), r.t., 24 h.
[b] [1,3-Bis(diphenylphosphino)propane]dichloronickel(II).
[c] Isolated yield.

3. Conclusion

In conclusion, we have presented the synthesis and structural study of ten nickel(II) Schiff base complexes. The crystal structures of the presented complexes show, that nickel atoms in all compounds have a distorted square planar coordination geometry. The complex molecules which contain imidazole, substituted imidazoles or 3-hydroxymethylpyridine ligands act as a supramolecular reagent for a building of the hydrogen bonding coordination networks.

The catalytic activity of the six Ni(II) complexes was examined in the Kumada–Corriu cross-coupling reaction. Three of them exhibited a good catalytic activity. On the other hand, other complexes which contain imidazole ring show a lower catalytic activity. This is probably due to the fact that hydrogen atom attached to nitrogen atom could be removed by phenylmagnesium bromide, resulting in the structure change.

4. Experimental

4.1. General

All the chemicals used were of reagent grade purity (Aldrich or Sigma, Acros Organics, Alfa-Aesar, Merck and Mikrochem Trade) and used without further purification. Carbon, hydrogen and nitrogen contents were determined by microanalytical methods (Thermo Electron Flash EA 1112). Electron spectra (9000–50 000 cm^{-1}) of the powdered samples in Nujol mulls were recorded at room temperature on a Specord 200 spectrophotometer (Carl Zeiss Jena). Infrared spectra in the region 400–4000 cm^{-1} were recorded on a Nicolet 5700 FT-IR spectrometer (Thermo Scientific). Spectra of the solid samples were obtained by the ATR technique at room temperature. Melting points were measured on a Melting Point B-540 apparatus (Büchi) and stayed uncorrected. ^{1}H NMR spectra were recorded on a Varian VRX-300 spectrometer (^{1}H, 300 MHz) and Varian INOVA-600 spectrometer (^{1}H, 600 MHz) in $CDCl_3$, d_8-THF and C_6D_6 using TMS as the internal standard. TLC analysis was carried out using TLC Silica gel 60

F254 (aluminum sheets, Merck) and visualized by UV light or with permanganate solution followed by heating. Flash column chromatography (FCC) was performed on Büchi system (Pump Manager C-615 and Fraction Collector C-660) using Normasil 60 silica gel (0.040–0.063 mm) (VWR). All solvents were dried and distilled according to conventional methods. THF was stored over molecular sieves and handled under inert atmosphere.

4.2. Synthesis of the complexes

4.2.1. Preparation of Schiff base H_2L

We added salicylaldehyde (22.38 g; 0.183 mol) to 2-hydroxyaniline (20 g; 0.183 mol) dissolved in acetonitrile (50 mL) and the resulting solution was refluxed for 20 min, during which the color turned yellow, and the red-orange microcrystalline solid precipitated. The solution was left to cool down, then it was filtered and the solid was washed with cold methanol and air dried. Yield (85%; 33.2 g).

4.2.2. [Ni(L)(PPh_3)](**5a**)

We added a solution of nickel(II) acetate tetrahydrate (0.497 g; 0.002 mol) in MeOH (30 mL) and solid PPh_3 (0.524 g; 0.002 mol) to a solution of Schiff base H2L (0.426 g; 0.002 mol) in MeCN (30 mL). The resulting solution was refluxed for 2 h and then left to evaporate slowly at ambient temperature. Well shaped red-brown crystals of complex **5a** suitable for single crystal X-ray structure analysis were collected after few days by filtration, washed with methanol and finally dried at ambient temperature.

Yield: 78%, ^{1}H NMR (600 MHz, C_6D_6): δ = 8.04 (s, 1H), 7.93 (br s, 6H), 7.31 (d, 1H, J = 8.2 Hz), 7.11 (d, 1H, J = 7.9 Hz), 7.09–7.02 (m, 9H), 6.99 (dd, 1H, J = 8.5, 6.9 Hz), 6.96 (dd, 1H, J = 8.2, 7.1 Hz), 6.88 (d, 1H, J = 8.2 Hz), 6.62 (d, 1H, J = 8.5 Hz), 6.57 (dd, 1H, J = 7.9, 6.9 Hz), 6.55 (1H, dd, J = 8.2, 7.1 Hz); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.0, 163.6, 148.4, 139.7, 135.0 (m, 6×C), 133.2, 132.5, 130.5 (3×C), 129.9 (only seen in HMBC, 3×C), 128.8, 128.6 (6×C), 122.4, 121.0, 118.6, 115.7, 114.7 (2×C); Elemental *Anal.* Calc.: C, 69.96; H, 4.55; N, 2.63; Found: C, 69.72; H, 4.72; N, 2.85%. IR (ATR) cm^{-1}: ν(C═N) 1606 s, ν(C—O) 1311 m, ν(Ni—P) 1098 s, ν(Ni—O) 527 s, ν(Ni—N) 454 s, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 500, 21 250.

4.2.3. [Ni(L)(Im)] (**5b**)

This red compound was prepared by the same procedure as for **5a** using imidazole (0.136 g; 0.002 mol) instead of triphenylphosphine.

Yield: 75%, ^{1}H NMR (600 MHz, d_8-THF): δ = 12.18 (br s, 1H), 8.50 (br s, 1H), 7.81 (br s, 1H), 7.65 (dd, 1H, J = 8.1, 1.3 Hz), 7.44 (dd, 1H, J = 8.0, 1.7 Hz), 7.12 (br s, 1H), 7.11 (ddd, 1H, J = 8.4, 6.8, 1.7 Hz), 7.06 (br s, 1H), 6.85 (dd, 1H, J = 8.4, 0.9 Hz), 6.84 (ddd, 1H, J = 8.1, 7.0, 1.3 Hz), 6.58 (dd, 1H, J = 8.1, 1.0 Hz), 6.55 (ddd, 1H, J = 8.0, 6.8, 0.9 Hz), 6.39 (ddd, 1H, J = 8.1, 7.0, 1.0 Hz); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.3, 164.5, 150.3, 141.3, 137.0, 133.4, 132.9, 128.8, 126.3, 122.4, 122.2, 118.0, 116.7, 115.7, 115.0, 114.4; Elemental *Anal.* Calc.: C, 56.86; H, 3.88; N, 12.43; Found: C, 56.99; H, 3.48; N, 12.56%. IR (ATR) cm^{-1}: ν(C═N) 1603 s, ν(C—O) 1302 m, ν(Ni—O) 523 s, ν(Ni—N) 447 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 000, 22 100.

4.2.4. [Ni(L)(4-Me-piperidine)] (**5c**)

This red compound was prepared by the same procedure as for **5a** using 4-methylpiperidine (0.198 g; 0.002 mol) instead of triphenylphosphine.

Yield: 72%, (600 MHz, $CDCl_3$): δ = 8.04 (s, 1H), 7.46 (dd, 1H, J = 8.0, 1.3 Hz), 7.32 (dd, 1H, J = 7.8, 1.6 Hz), 7.17 (ddd, 1H, J = 8.5, 6.8, 1.6 Hz), 6.96 (ddd, 1H, J = 8.1, 7.2, 1.3 Hz), 6.85 (dd, 1H, J = 8.5, 1.1 Hz), 6.67 (dd, 1H, J = 8.1, 1.2 Hz), 6.63 (ddd, 1H, J = 7.8, 6.8, 1.1 Hz), 6.50 (ddd, 1H, J = 8.0, 7.2, 1.2 Hz), 3.77–3.65 (m, 2H), 2.84–2.71 (m, 2H), 1.75–1.66 (m, 2H), 1.62–1.51 (m, 1H), 1.50 (tt, 1H, J = 12.2, 2.5 Hz), 1.15–1.04 (m, 2H), 0.91 (d, 3H, J = 6.5 Hz); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.6, 163.2, 148.5, 139.4, 132.7, 132.5, 128.5, 121.0 (2×C), 117.1, 115.5, 114.5, 113.8, 47.8 (2×C), 34.9 (2×C), 30.3, 22.2; Elemental *Anal.* Calc.: C, 62.00; H, 5.75; N, 7.61; Found: C, 61.87; H, 5.61; N, 7.85%. IR (ATR) cm^{-1}: ν(C═N) 1604 s, ν(C—O) 1295 s, ν(Ni—O) 545 s, ν(Ni—N) 445 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 500, 22 200.

4.2.5. [Ni(L)(4-Bn-pyridine)] (**5d**)

This red compound was prepared by the same procedure as for **5a** using 4-benzylpyridine (0.338 g; 0.002 mol) instead of triphenylphosphine.

Yield: 73%, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.55 (br s, 2H), 8.14 (br s, 1H), 7.53 (d, 1H, J = 7.8 Hz), 7.38 (d, 1H, J = 7.6 Hz), 7.34–7.30 (m, 2H), 7.28–7.24 (m, 1H), 7.18 (dd, 1H, J = 8.4, 6.8 Hz), 7.17–7.13 (m, 4H), 6.97 (dd, 1H, J = 8.1, 6.9 Hz), 6.88 (d, 1H, J = 8.4 Hz), 6.72 (d, 1H, J = 8.1 Hz), 6.66 (dd, 1H, J = 7.6, 6.8 Hz), 6.53 (dd, 1H, J = 7.8, 6.9 Hz), 3.96 (br s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.2, 162.9, 149.4, 140.0, 132.9, 132.7, 129.1 (2×C), 128.9 (2×C), 128.6, 127.0, 121.2, 120.9, 117.4, 115.8, 114.7, 114.0, 41.3; Elemental *Anal.* Calc.: C, 68.38; H, 4.59; N, 6.38; Found: C, 68.55; H, 4.88; N, 6.12%. IR (ATR) cm^{-1}: ν(C═N) 1593 s, ν(C—O) 1295 s, ν(Ni—O) 548 s, ν(Ni—N) 445 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 400, 22 200.

4.2.6. [Ni(L)(2-Me-5-Et-pyridine)] (**5e**)

This red compound was prepared by the same procedure as for **5a** using 2-methyl-5-ethylpyridine (0.242 g; 0.002 mol) instead of triphenylphosphine.

Yield: 80%, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.25 (s, 1H), 8.09 (s, 1H), 7.55 (dd, 1H, J = 8.1, 1.2 Hz), 7.48 (br d, 1H, J = 7.7 Hz), 7.37 (dd, 1H, J = 7.9, 1.6 Hz), 7.14 (ddd, 1H, J = 8.6, 6.9, 1.6 Hz), 7.14 (br d, 1H, J = 7.7 Hz), 6.96 (ddd, 1H, J = 8.2, 7.1, 1.2 Hz), 6.73 (dd, 1H, J = 8.6, 0.9 Hz), 6.68 (dd, 1H, J = 8.2, 1.0 Hz), 6.64 (ddd, 1H, J = 7.9, 6.9, 0.9 Hz), 6.53 (ddd, 1H, J = 8.1, 7.1, 1.0 Hz), 3.67 (s, 3H), 2.71 (br q, 2H, J = 7.7 Hz), 1.30 (br t, 3H, J = 7.7 Hz); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.8, 163.2, 158.1, 150.4, 149.1, 139.5, 137.6, 137.3, 132.8, 132.7, 128.6, 125.2, 120.9, 120.7, 117.3, 115.5, 114.6, 113.8, 25.6, 25.1, 14.8. Elemental *Anal.* Calc.: C, 64.49; H, 5.15; N, 7.16; Found: C, 64.34; H, 5.51; N, 7.44%. IR (ATR) cm^{-1}: ν(C═N) 1600 s, ν(C—O) 1311 s, ν(Ni—O) 545 m, ν(Ni—N) 445 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 250, 21 200.

4.2.7. [Ni(L)(3-hydroxymethylpyridine)] (**5f**)

This red compound was prepared by the same procedure as for **5a** using 3-hydroxypyridine (0.218 g; 0.002 mol) instead of triphenylphosphine.

Yield: 75%, Elemental *Anal.* Calc.: C, 60.21; H, 4.25; N, 7.39; Found: C, 60.48; H, 4.01; N, 7.46%. IR (ATR) cm^{-1}: ν(C═N) 1606 s, ν(C—O) 1313 s, ν(Ni—O) 544 s, ν(Ni—N) 449 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 350, 21 500.

4.2.8. [Ni(L)(2-Me-benzimidazole)] (**5g**)

This red compound was prepared by the same procedure as for **5a** using 2-methylbenzimidazole (0.624 g; 0.002 mol) instead of triphenylphosphine.

Yield: 70%, Elemental *Anal.* Calc.: C, 62.73; H, 4.26; N, 10.45; Found: C, 62.56; H, 4.12; N, 10.68%. IR (ATR) cm^{-1}: ν(C═N) 1582 s, ν(C—O) 1309 s, ν(Ni—O) 526 m, ν(Ni—N) 448 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 200, 22 400.

*4.2.9. [Ni(L)(2,6-Me$_2$-pyridine)] (**5h**)*

This red compound was prepared by the same procedure as for **5a** using 2,6-dimethylpyridine (0.214 g; 0.002 mol) instead of triphenylphosphine.

Yield: 75%, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 7.56 (dd, 1H, J = 8.2, 1.2 Hz), 7.52 (t, 1H, J = 7.6 Hz), 7.36 (dd, 1H, J = 8.0, 1.9 Hz), 7.11 (ddd, 1H, J = 8.2, 6.9, 1.9 Hz), 7.09 (d, 2H, J = 7.6 Hz), 6.95 (ddd, 1H, J = 7.9, 7.2, 1.2 Hz), 6.66 (dd, 1H, J = 8.2, 1.0 Hz), 6.65 (dd, 1H, J = 7.9, 1.2 Hz), 6.62 (ddd, 1H, J = 8.0, 6.9, 1.0 Hz), 6.52 (ddd, 1H, J = 8.2, 7.2, 1.2 Hz), 4.17 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 165.0, 163.4, 160.2 (2×C), 148.9, 139.4, 138.1, 132.6 (2×C), 128.5, 122.4 (2×C), 121.0, 120.6, 117.4, 115.3, 114.3, 113.7, 26.5 (2×C); Elemental *Anal.* Calc.: C, 63.71; H, 4.81; N, 7.43; Found: C, 63.52; H, 4.75; N, 7.59%. IR (ATR) cm^{-1}: ν(C═N) 1603 s, ν(C—O) 1311 s, ν(Ni—O) 545 s, ν(Ni—N) 440 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 250, 21 700.

*4.2.10. [Ni(L)(4-Me-pyridine)] (**5i**)*

This red compound was prepared by the same procedure as for **5a** using 4-methylpyridine (0.186 g; 0.002 mol) instead of triphenylphosphine.

Yield: 75%, ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.52 (br s, 2H), 8.16 (br s, 1H), 7.54 (br s, 2H), 7.54 (d, 1H, J = 7.9 Hz), 7.39 (d, 1H, J = 7.8 Hz), 7.20 (dd, 1H, J = 8.5, 6.6 Hz), 6.98 (dd, 1H, J = 8.0, 7.0 Hz), 6.90 (d, 1H, J = 8.5 Hz), 6.74 (d, 1H, J = 8.0 Hz), 6.66 (dd, 1H, J = 7.8, 6.6 Hz), 6.54 (dd, 1H, J = 7.9, 7.0 Hz), 2.38 (br s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.3, 163.0, 149.8, 149.4, 140.1, 132.9, 132.7, 128.6, 125.2, 121.2, 121.0, 117.4, 115.8, 114.7, 114.0, 21.3; Elemental *Anal.* Calc.: C, 62.86; H, 4.44; N, 7.72; Found: C, 62.55; H, 4.68; N, 7.81%. IR (ATR) cm^{-1}: ν(C═N) 1594 s, ν(C—O) 1322 s, ν(Ni—O) 546 s, ν(Ni—N) 450 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 350, 22 100.

*4.2.11. [Ni(L)(2-^{i}Pr-benzim)]·MeOH (**5j**)*

This red compound was prepared by the same procedure as for **5a** using 2-izopropylbenzimidazole (0.320 g; 0.002 mol) instead of triphenylphosphine.

Yield: 76%, Elemental *Anal.* Calc.: C, 64.37; H, 5.45; N, 9.09; Found: C, 64.38; H, 5.12; N, 9.21%. IR (ATR) cm^{-1}: ν(C═N) 1601 s, ν(C—O) 1312 s, ν(Ni—O) 545 s, ν(Ni—N) 445 m, UV–Vis (NUJOL) λ_{max} cm^{-1}: 23 750, 22 200.

4.3. X-ray crystallography

Data collection for **5a**, **5b** and **5e**–**5i** were collected on a Bruker-Nonius KappaCCD diffractometer at 150 K or Oxford Diffraction Xcalibur S CCD diffractometer at 293 K, with graphite monochromated Mo Kα radiation. Intensity data for **5d** was collected using a Bruker APEX II CCD Ultra diffractometer with a micro-focused rotating anode (Mo Kα radiation) and multilayer monochromator at 100 K. The diffraction intensities were corrected for Lorentz and polarization factors. The semi-empirical absorption corrections were made by multi-scans method using SADABS or SCALE3 ABSPACK algorithm within CRYSALISPRO. The structures were solved by the direct or charge-flipping methods using programs SHELXT [27], SIR2014 [28], OLEX2.solve [29] or SUPERFLIP [30], and refined by the full-matrix least squares procedure with SHELXL [31] (ver. 2014/7) or CRYSTALS [32] (ver. 14.61). Geometrical analysis was performed using SHELXL or CRYSTALS. The positions of all hydrogen atoms have been constrained for all compounds using AFIX (SHELXL) or RIDE (CRYSTALS) commands.

The anionic ligand L_1 of **5a**, **5e**, **5g**, **5h** and **5j**, and full complex molecule of **5d** are positional disorders. The positionally disordered parts were restrained using SAME and/or SADI, EXYZ a RIGU commands in SHELXL.

Final crystal data and structure refinement parameters are given in Supplementary Table S2. The crystal structures were drawn using the OLEX2 program [33]. The crystallographic data for **5a**, **5b**, and **5d**–**5j** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC Nos. 1406133–1406143.

4.4. Kumada–Corriu cross-coupling reactions with the selected nickel (II) complexes; General procedure

A Schlenk tube was charged with a catalyst **5** (2 mol%, 0.04 mmol), sealed with a rubber septum, evacuated and filled with argon. THF (2 mL) was added followed by aryl bromide **6** (2 mmol). After stirring for 10 min, the solution of phenylmagnesium bromide (**7**) (4 mmol, 1 M in THF) was added drop-wise via syringe, and stirring continued at ambient temperature for 24 h. Upon reaction completion, sat. aq. NH_4Cl solution was added, and the mixture was stirred for additional 10 min. Then, the mixture was extracted with Et_2O (3 × 50 mL). Combined organic layers were dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The product was isolated by column chromatography (hexanes/ethyl acetate) to provide desired coupled product **8**. The isolated yields of **8a**–**c**, depending on the catalyst, are summarized in Table 1.

*4.4.1. 4-Methoxybiphenyl (**8a**)*

The general procedure above was followed using 4-bromoanisole (**6a**) (250 μL, 2 mmol) and phenylmagnesium bromide (**7**) (4 mL, 4 mmol, 1 M in THF). FCC on silica gel (hexanes/ethyl acetate, 98:2) provided product **8a** as a colorless solid in various yields, depending on the catalyst: Yields/catalyst: [210 mg (57%)/$NiCl_2$(dppp); 258 mg (70%)/**5a**; 180 mg (49%)/**5b**; 240 mg (65%)/**5c**; 258 mg (70%)/**5d**; 156 mg (42%)/**5g**; 154 mg (42%)/**5j**].

Mp 88–89 °C [Mp 90–91 °C (EtOH)] [34].

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.53 (m, 4H), 7.46–7.41 (m, 2H), 7.35–7.32 (m, 1H), 7.03–6.98 (m, 2H), 3.87 (s, 3H).

*4.4.2. 1-Phenylnaphthalene (**8b**)*

The general procedure above was followed using 1-bromonaphthalene (**6b**) (280 μL, 2 mmol) and phenylmagnesium bromide (**7**) (4 mL, 4 mmol, 1 M in THF). FCC on silica gel (hexanes/ethyl acetate, 98:2) provided product **8b** as a colorless oil [35] in various yields, depending on the catalyst: Yields/catalyst: [330 mg (81%)/**5a**; 320 mg (78%)/**5d**].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.94–7.93 (m, 1H), 7.89–7.88 (m, 1H), 7.63–7.61 (m, 2H), 7.56–7.49 (m, 3H), 7.48–7.45 (m, 4H), 7.38–7.36 (m, 1H).

*4.4.3. 3-Phenylpyridine (**8c**)*

The general procedure above was followed using 3-bromopyridine (**6c**) (195 μL, 2 mmol) and phenylmagnesium bromide (**7**) (4 mL, 4 mmol, 1 M in THF). FCC on silica gel (hexanes/ethyl acetate, 75:25) provided product **8c** as a colorless oil [35] in various yields, depending on the catalyst: Yields/catalyst: [185 mg (60%)/**5a**; 192 mg (62%)/**5d**].

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.85 (dd, 1H, J = 2.4, 0.8 Hz), 8.58 (dd, 1H, J = 4.8, 1.7 Hz), 7.84 (ddd, 1H, J = 7.9, 2.4, 1.7 Hz), 7.56–7.55 (m, 2H), 7.47–7.44 (m, 2H), 7.38 (tt, 1H, J = 7.4, 1.2 Hz), 7.33 (ddd, 1H, J = 7.9, 4.8, 0.8 Hz).

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Appendix A. Supplementary data

CCDC 1406133–1406143 contains the supplementary crystallographic data for **5a**, **5b**, and **5d**–**5j**. These data can be obtained free 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.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.05.037.

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