Nickel N-heterocyclic carbene complexes in homogeneous catalysis

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Chapter 5

N-donor functionalized N-heterocyclic carbene nickel(II) complexes in the Kumada coupling[†]

Abstract. *The synthesis and characterization of novel nickel(II) complexes bearing two bidentate N-heterocyclic carbene ligands functionalized with anionic N-donor moieties are described. Two different N-donor groups are employed, namely amido and benzimidazolato moieties. The solid-state structures of three of these complexes have been determined by X-ray crystallography. The amido-functionalized low-spin, square-planar Ni(II) complexes exhibit a cis-geometry around the metal center, while the benzimidazolato-functionalized complex crystallizes as the trans isomer. The activity of these novel complexes in the Kumada cross-coupling of phenylmagnesium chloride with 4-chloroanisole and 4-fluoroanisole was investigated. One of the benzimidazolato-functionalized complexes shows the highest activity in this reaction reported to date, yielding the desired product in quantitative yields within 30 minutes (4-chloroanisole), or 150 minutes (4-fluoroanisole) with only 1 mol% catalyst.*

[†] Based on: J. Berding, T. F. van Dijkman, M. Lutz, A. L. Spek, E. Bouwman, *Dalton Trans.*, **2009**, 6948

5.1 Introduction

The study and application of N-heterocyclic carbenes (NHCs) have increased rapidly in recent years, most notably for their use as spectator ligands in homogeneous catalysis.[1-4] For example, palladium NHC complexes have been used as versatile catalysts for a number of C–C couplings reactions, such as the Heck, Stille, Suzuki and Sonogashira reactions, which are of great importance for organic chemistry.[5] Though not as popular as their palladium analogues, nickel NHC complexes have also been investigated for a number of C–C couplings reactions. One reaction in which nickel complexes perform particularly well, compared to palladium, is the Kumada cross-coupling of aryl halides with aryl Grignard reagents. This reaction, discovered simultaneously by two groups in 1972,[6, 7] may be an economically attractive alternative to other cross-coupling reactions, as it uses cheap starting materials and only has magnesium salts as by-products, even though it lacks the functional group tolerance.

An early report of the use of N-heterocyclic carbenes in the nickel-catalyzed Kumada coupling from the group of Herrmann revealed that imidazolium salts with bulky N-substituents in combination with $Ni(acac)_2$ generates an active catalyst for the coupling of aryl chlorides with aryl Grignard reagents.[8] The results on the Kumada coupling with nickel complexes of chelating benzimidazole-based dicarbenes is described in Chapter 4. Other groups investigated chelating ligands or ligand precursors consisting of one (or more) NHC and one (or more) hemi-labile group for the same reaction.[9-12] In most cases these chelating ligands are neutral, leading to either cationic Ni(II) complexes or complexes with coordinated counterions, such as halides. A recent review describing donor-functionalized NHC complexes of group 9 and 10 metals, reveals that NHC ligands with anionic side groups are quite uncommon.[4] A number of nickel(II) complexes of chelating ligands with N-heterocyclic carbenes and amido functionalities has recently been reported to form active catalysts in the Suzuki cross-coupling.[13] The present chapter describes the Kumada coupling using nickel complexes of NHC ligands with various pendant anionic N-donor moieties.

5.2 Results and Discussion

5.2.1 Synthesis of ligand precursors

An overview of the ligand precursors used in this study is shown in Figure 5.1. Ligand precursors **1** and **2** were synthesized following an adaptation of literature procedures,[14] by reacting N-substituted (benz)imidazoles with 2-chloro-N-phenylacetamide. Novel ligand precursors **3** and **4** were obtained in good yield by a facile quaternization of N-benzyl(benz)imidazole with 2-chloromethylbenzimidazole in hot 1,4-dioxane. The ^{1}H and ^{13}C NMR spectra of **1 – 4** show the characteristic

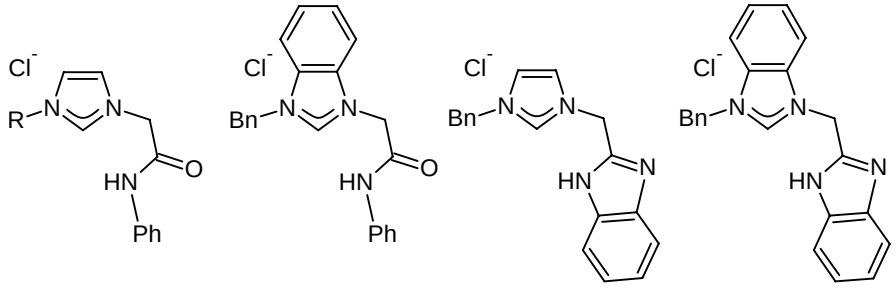


Figure 5.1. Overview of the ligand precursors used in this study.

imidazolium NCHN resonances around 9.5 and 140 ppm, respectively. The formation of **1** – **4** was further confirmed with ESI-MS, the spectra showing the parent peak for the respective $[M - Cl]^+$ fragments.

5.2.2 Synthesis and characterization of the nickel complexes

Treatment of ligand precursors **1** – **4** with potassium carbonate in the presence of nickel(II) chloride in hot DMF yields yellow, diamagnetic complexes **5** – **8**, shown in Figure 5.2. All complexes are air- and moisture stable and could be isolated after treatment with water in air. In principle such complexes can be obtained as either the *cis* or the *trans* isomer. It was shown for complex **5b** that the ratio of the two isomers depends on the polarity of the solvent: more polar solvents yield a higher amount of the *cis* complex, while in apolar solvents the complex isomerizes to the *trans* isomer.[13]

In accordance with the square-planar geometry of the nickel(II) complexes, the ^{1}H NMR spectra of all complexes show sharp signals in the diamagnetic region. The characteristic NCHN signals of the precursors are absent from the NMR spectra of these complexes, indicating carbene generation. In addition, the NH signals are no

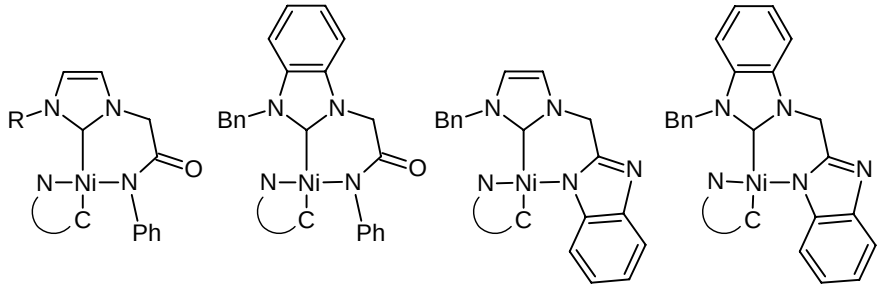


Figure 5.2. Schematic representation of the nickel complexes 5-8. Only the *trans* isomer is drawn.

longer present in the spectra of the complexes, reflecting bidentate coordination of the ligand. The ^{1}H NMR spectrum of **7** in DMSO-d_6 is indicative of a 0.6:0.4 mixture of *trans* and *cis* isomers (Figure 5.3). No attempts were made to assign the peaks to

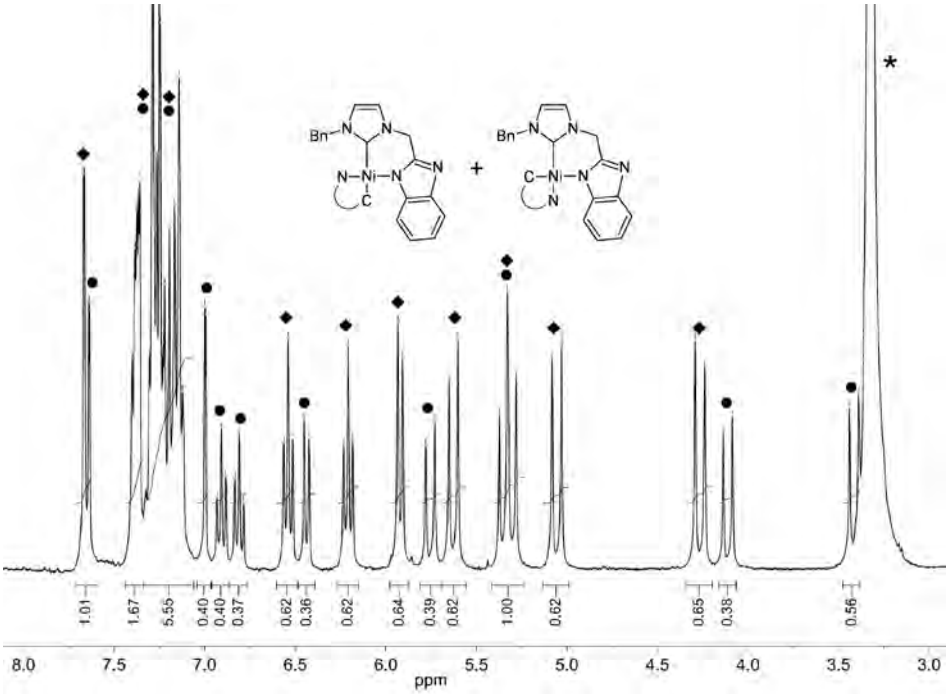


Figure 5.3. ^{1}H NMR spectrum of complex **7** in DMSO. The peaks of two different isomers are marked with (♦) and (●). The residual water peak is marked with (*).

their respective isomers. In $CDCl_3$ only one isomer of **7** is present, presumably with the *trans* configuration. The other nickel compounds appear to be present as a single isomer in DMSO-d_6. The ^{1}H NMR spectra of all complexes show splitting of the

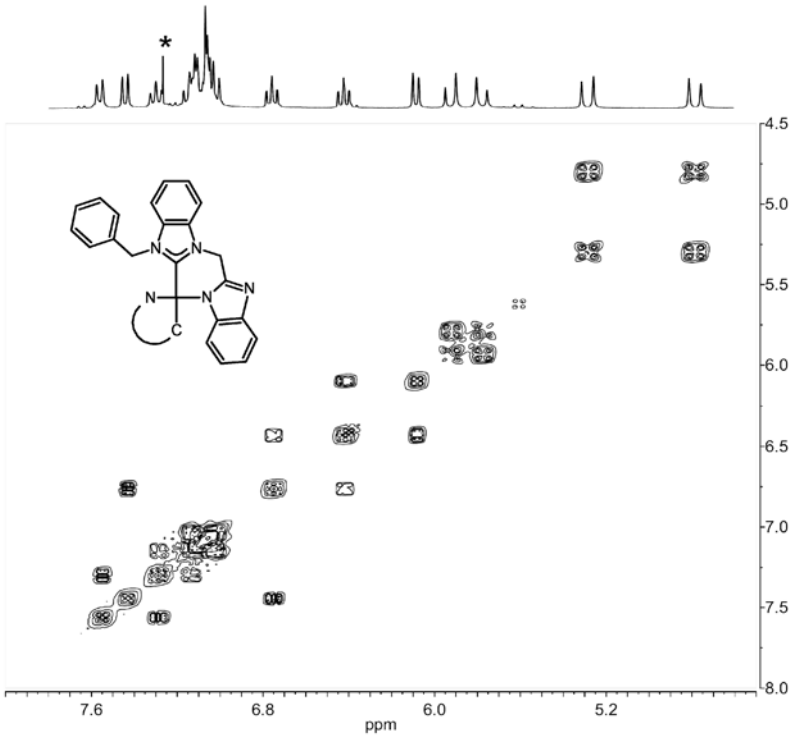


Figure 5.4. ^{1}H COSY NMR spectrum of complex **8** in $CDCl_3$. The residual solvent peak is marked with (*).

backbone-CH_2 resonances, apparently caused by the rigidity of the structure in solution. The resonances of the benzimidazolato group of complex **8** are split over a range of 1.5 ppm and could be assigned with the aid of COSY NMR spectroscopy (Figure 5.4). The ESI-MS spectra of the complexes show the $[M + H]^+$ parent peak for all complexes.

5.2.3 Description of the structures

Single crystals suitable for X-ray crystal structure determination were obtained from methanol (**5a**), by slow diffusion of hexane into a concentrated solution of the compound in dichloromethane (**6**), or by slow diffusion of diethyl ether into a concentrated solution of the compound in chloroform (**8**). Molecular plots of **5a** and **6** are shown in Figure 5.5, selected bond lengths, angles and torsion angles are given in Table 5.1.

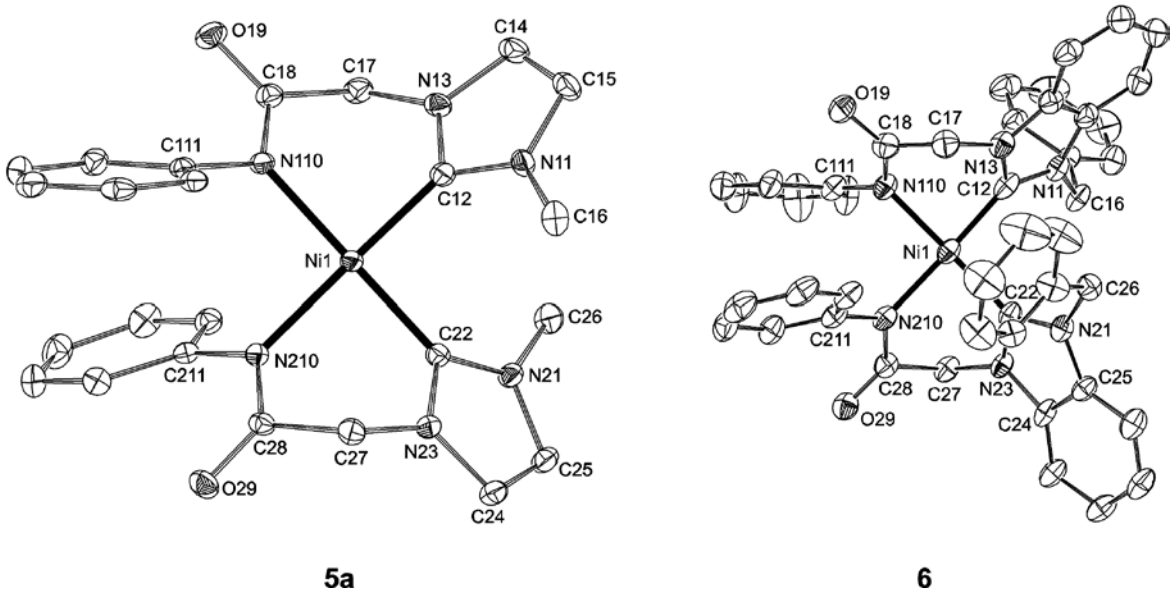


Figure 5.5. Displacement ellipsoid plots (30% probability level) of **5a** and **6** in the crystal. In **5a** only one of two independent metal units is shown. In both cases, hydrogen atoms and solvent molecules are omitted for clarity.

The two independent metal entities of **5a**, as well as complex **6**, have an approximate twofold symmetry, which is only broken by slightly different conformations of the phenyl rings. The nickel ions in these complexes are in a slightly distorted square-planar geometry with *cis*-angles that range between 85.60(14) and 94.71(15)°. The ligands are bound in a *cis* configuration. The Ni–C and Ni–N bond distances are within the expected range.[13] The carbene (benz)imidazol-2-ylidene rings are twisted with respect to the coordination plane by 45.08(11) – 53.5(2)°. The six-membered chelate rings adopt a boat conformation in all cases.

Table 5.1. Selected bond lengths (Å), angles, and torsion angles (°) for **5a** and **6**. [Second independent molecule of **5a** in brackets] and parameters for the hydrogen bonding in **5a**.

	5a	**6**
Ni1 – N110	1.9524(18) [1.9338(18)]	1.926(3)
Ni1 – N210	1.9511(18) [1.9582(18)]	1.952(3)
Ni1 – C12	1.849(2) [1.845(2)]	1.852(4)
Ni1 – C22	1.867(2) [1.849(2)]	1.875(3)
C14 – C15	1.337(4) [1.340(4)]	1.387(5)
C24 – C25	1.341(3) [1.349(3)]	1.400(5)
N110 – Ni1 – N210	92.57(8) [94.12(8)]	91.89(12)
N110 – Ni1 – C12	88.44(9) [88.14(9)]	85.60(14)
N210 – Ni1 – C22	88.05(9) [87.87(8)]	87.69(14)
C12 – Ni1 – C22	91.02(10) [89.92(9)]	94.71(15)
N11 – C12 – N13	105.2(2) [104.98(19)]	105.8(3)
N21 – C22 – N23	104.74(19) [104.47(19)]	106.3(3)
N110 – Ni1 – C12 – N13	–43.82(18) [–46.37(17)]	53.0(3)
N210 – Ni1 – C22 – N23	–42.76(18) [–43.98(19)]	42.0(3)

5a	D-H [Å]	H···A [Å]	D···A [Å]	D-H···A [°]
O5-H5O···O19	0.96	1.80	2.740(2)	168
O6-H6O···O29	0.93	1.75	2.675(2)	173
O7-H7O···O49	0.89	1.86	2.731(3)	166
O8-H8O···O19	1.05	1.70	2.737(3)	169
O9-H9A···O8	1.02	1.98	2.934(3)	154
O9-H9B···O39	0.96	1.94	2.797(3)	175

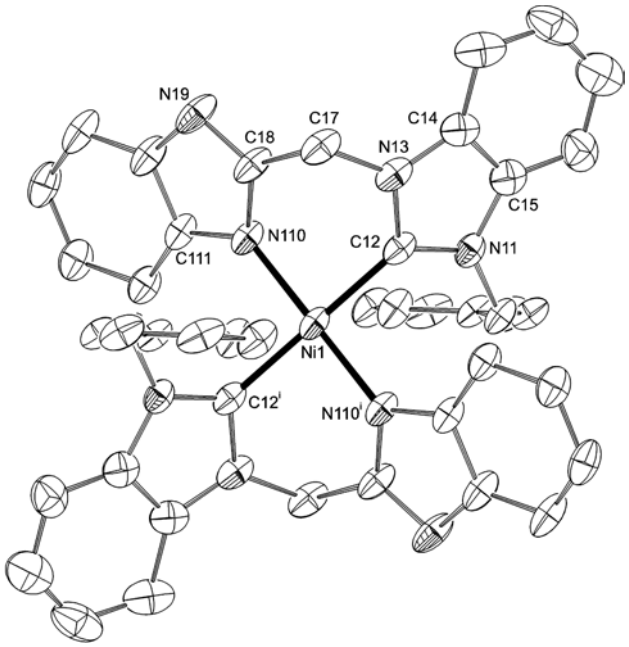


Figure 5.6. Displacement ellipsoid plot (30% probability level) of **8**. Only one of the independent metal complexes is shown. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry operation i: –x, –y, –z.

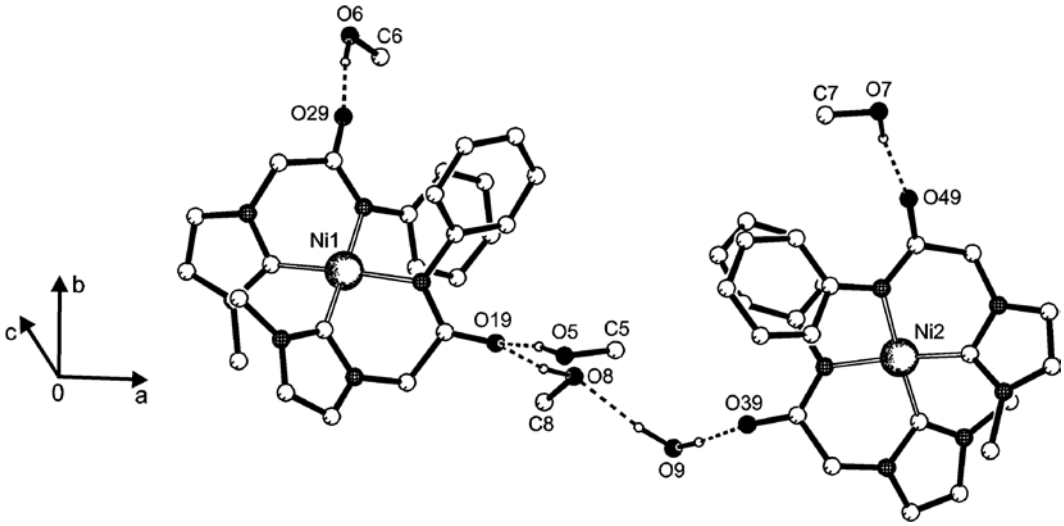


Figure 5.7. Discrete hydrogen-bonded aggregate of metal complexes, methanol and water molecules in the asymmetric unit of **5a**. C-H hydrogen atoms are omitted for clarity. Geometrical characterizations of the hydrogen bonds are provided in Table 5.1.

The asymmetric unit of **5a** contains two independent metal complexes, four methanol and one water molecule, which are connected by O-H···O hydrogen bonds (Figure 5.7). In particular, hydrogen bonding occurs through the carbonyl functionalities of the ligands. Oxygen O29 is acceptor of a hydrogen bond from a methanol molecule, while oxygen O19 interacts with two methanol molecules, one of which is linked to the water molecule. The latter connects to the other nickel complex through oxygen O39. Finally, oxygen O49 is a hydrogen bond acceptor of the fourth methanol molecule.

Two independent metal complexes are present in the crystal structure of **8**, which are both located on inversion centers. The asymmetric unit thus contains two

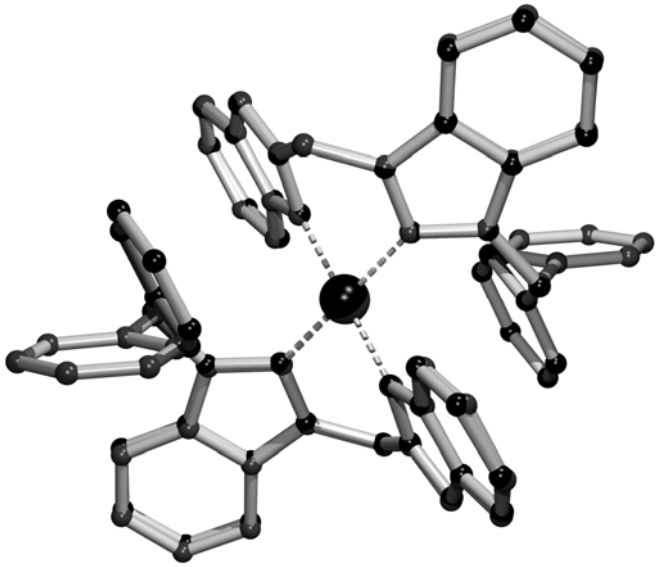


Figure 5.8. Quaternion fit of the two independent metal complexes in the crystal structure of **8**, based on the six-membered chelate ring. Both independent molecules are located on an inversion center. The calculation was performed with the program PLATON.

Table 5.2. Selected bond lengths (Å), angles, and torsion angles (°) for **8**. [Second independent molecule in brackets].

Ni1 – N110	1.8840(13) [1.8776(12)]
Ni1 – C12	1.9133(19) [1.9070(15)]
C14 – C15	1.370(3) [1.389(2)]
N110 – Ni1 – C12	86.41(7) [86.59(6)]
N110 – Ni1 – C12^{i}	93.59(7) [93.41(6)]
N11 – C12 – N13	105.58(16) [106.33(13)]
N110 – Ni1 – C12 – N13	42.19(14) [43.54(12)]

different half molecules. A molecular plot is shown in Figure 5.6 and a selection of bond lengths, angles and torsion angles is listed in Table 5.2.

Due to the inversion symmetry of the metal complexes, a *trans* ligand geometry is present. The nickel ion has an almost square-planar geometry, with Ni–C bond lengths of 1.9070(15) – 1.9133(19) Å. These distances are significantly longer than the Ni–C distances found for the *cis* complexes **5a** and **6** and are slightly longer than those found in *trans*-[(NHC)$_2$NiI$_2$] complexes, in which NHC is a monodentate benzimidazole-based N-heterocyclic carbene.[15] The Ni–N$^-$ bond lengths of compound **8** of 1.8776(12) – 1.8840(13) Å are shorter than in other Ni complexes with a N-deprotonated benzimidazole ligand, with distances of 1.9004(14)[16] and 2.0724(16) Å.[17] The carbene rings are twisted with respect to the NiC$_2$N$_2$ coordination plane by 45.46(9) and 46.01(7)°, while the N-coordinated benzimidazole rings are twisted by 42.46(11) and 44.39(8)°. The six-membered chelate rings adopt boat conformations. The two independent complexes in the asymmetric unit have roughly the same coordination environment around the nickel center. However, a significant difference is observed in the orientation of the benzyl side group. A superposition of the two molecules showing this difference is given in Figure 5.8. One of the orientations brings the benzyl aromatic ring in proximity of the nickel center, resulting in an

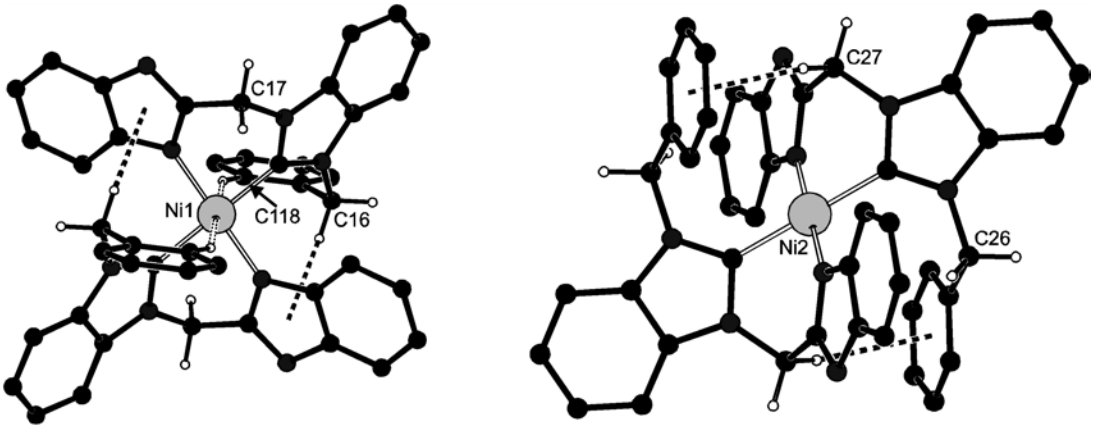
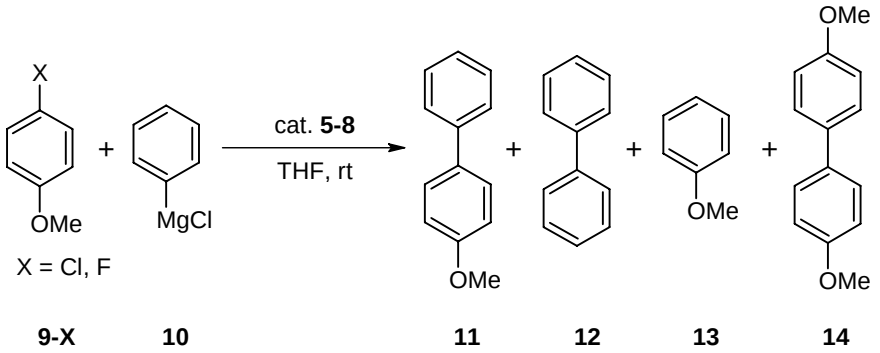


Figure 5.9. C-H···Ni and C-H···π interactions in the two independent molecules of **8**. H118···Ni1, 2.72 Å; C118···Ni1, 3.579(2) Å; C118-H118···Ni1, 151°; H16A···Cg, 2.54 Å; C16···Cg, 3.485(2) Å; C16-H16A···Cg, 161°; H27B···Cg, 2.65 Å; C27···Cg, 3.5420(19); C27-H27B···Cg, 150°.



Scheme 5.1. Products of the nickel-catalyzed Kumada cross-coupling of 4-haloanisole and phenylmagnesium chloride.

anagostic interaction between one *ortho* proton and the nickel ion (d(Ni···H = 2.72 Å, ∠(C-H···Ni) = 151°).[18] Similar observations were reported recently for square-planar nickel complexes containing phenylimidazole as a ligand.[19] The other orientation in the second independent metal complex allows a C-H···π interaction between one of the CH_2-bridges as donor and the benzyl aromatic ring as acceptor (Figure 5.9).

5.2.4 Catalytic studies

Complexes **5** – **8** were tested as catalysts in the Kumada coupling of 4-chloroanisole (**9-Cl**) with phenylmagnesium chloride (**10**) at room temperature (Scheme 5.1). The results of the catalytic experiments are summarized in Table 5.3. The reaction was monitored by taking samples at regular intervals and analysis by gas chromatography. A number of side products was identified. Apart from the desired product 4-methoxybiphenyl (**11**), varying amounts of biphenyl (**12**), anisole

Table 5.3. Nickel-catalyzed Kumada cross-coupling of 4-haloanisole and phenylmagnesium chloride at room temperature.[a]

		Time [b]	Yield (10^{-2} mmol) [c]			
Entry	Catalyst	(min)	**11**	**12**	**13**	**14**
1	**5a**	150	85	10	1	6
2	**5b**	75	87	13	3	4
3	**6**	150	90	15	2	3
4	**7**	20	99 (95)	3	0	0
5	**8**	12	97	6	0	2
6	**8** [d]	30	99	3	0	0
7	**8** [d,e]	150	98	5	0	1
8	(C^C)NiBr$_2$ [f]	< 840	99	6	0	0

[a] Reaction conditions: 0.03 mmol cat., 1.0 mmol 4-chloroanisole, 1.5 mmol phenylmagnesium chloride (25 wt% in THF), 1.0 mL THF, RT; [b] Time needed for full consumption of 4-haloanisole; [c] Yields determined by GC, average of two runs. Yields in parentheses are isolated yields; [d] 0.01 mmol cat.; [e] 4-fluoroanisole was used a substrate; [f] Dibromido-1,1′-dibenzyl-3,3′-(1,3-propanediyl)dibenzimidazol-2,2′-diylidenenickel(II), see Chapter 4.

(**13**) and bisanisole (**14**) were found to be present in the reaction mixtures.

Initially, the catalytic reactions were performed using commonly used conditions, *i.e.* a 0.03 : 1 : 1.5 ratio of nickel complex, 4-chloroanisole, and phenylmagnesium chloride in THF at room temperature (Table 5.3, entry 1 – 5).[8, 9, 20] Additionally, complex **8** was used at a lower catalyst loading of 1.0 mol% (entry 6) and it was used to couple 4-fluoroanisole (**9-F**) with phenylmagnesium chloride at the same low catalyst loading (entry 7).

The results of the catalytic reactions are summarized in Table 5.3 as the time needed to quantitatively consume the 4-haloanisole with the yields (in mmol) of the desired product and the side products. As the Grignard reagent was used in excess, and unreacted Grignard reagent cannot be detected on GC, the following constraints should apply (see Chapter 4): The sum of the amounts of **11**, **13** and twice the amount of **14** should be equal to 1 mmol, while the amount of **12** should not exceed half the amount of Grignard reagent that did not react to form **11**, which is equal to 0.5 × (1.5 mmol – the amount of **11**). Both requirements are met in all catalytic experiments.

All complexes **5** – **8** are catalytically active in the coupling of 4-chloroanisole with phenylmagnesium chloride. The time needed to consume all starting aryl halide and the selectivity, however, are strongly dependent on the ligand used. The catalysts **5** and **6** with the amide-substituted ligands need 75 to 150 minutes to complete the reaction, yielding the desired product in 85 to 90% yield. The complexes **7** and **8** with benzimidazole-substituted ligands are highly active, furnishing the product **11** in nearly quantitative yields in less than 20 minutes. A plot of the development of reagents and products in the reaction mixture in time using compound **8** (Table 5.3, entry 6) is shown in Figure 5.10. In this case side products **13** and **14** are not detected in the reaction mixture. A short induction time is observed.

Used at a lower catalyst concentration, compound **8** was able to couple the two reagents quantitatively within 30 minutes at room temperature, corresponding to an average turnover frequency of 200 mol·(mol cat.)$^{-1}$·h^{-1}. Moreover, even the less reactive 4-fluoroanisole could be coupled efficiently and nearly quantitatively in 150 minutes at the same 1 mol% catalyst concentration.

Compared to the catalytic results obtained with nickel catalysts with bidentate bisNHC ligands (Chapter 4), the new complexes with anionic (C^N$^-$) ligands perform remarkably well. The best performing bisNHC nickel catalyst reported in Chapter 4 was also able to reach quantitative conversion of the aryl chloride to the desired product; however, it required about 14 hours to complete the reaction (Table 5.3, entry 8).[21]

Several reports have been published on the nickel NHC catalyzed Kumada coupling of 4-chloroanisole (**9-Cl**) with phenylmagnesium chloride.[8-12, 20-23] As different conditions were used in different studies and furthermore, in most cases only the conversion and selectivity after a fixed time are given, comparison is difficult. The best performing nickel NHC complexes to date are the following. A

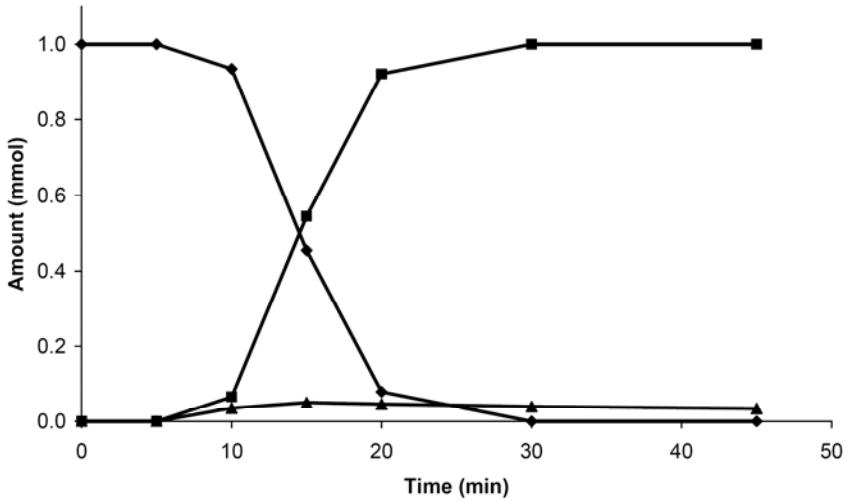


Figure 5.10. Evolution of the products in time of a typical catalytic experiment (Table 5.3, entry 6): (♦) 4-chloroanisole; (■) 4-methoxybiphenyl; (▲) biphenyl.

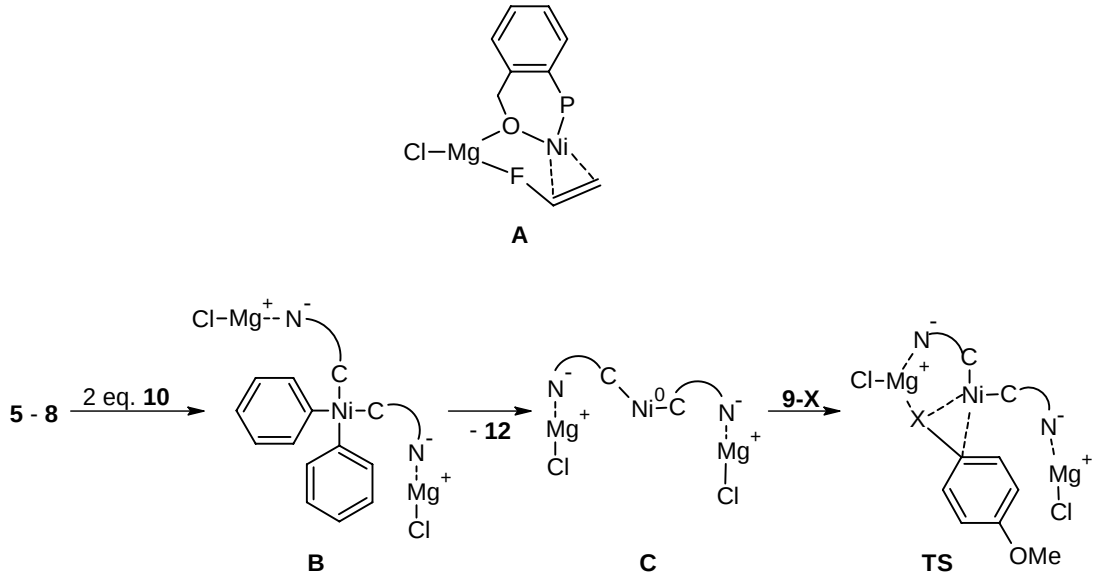
nickel complex bearing a phosphane-NHC (C^P) bidentate ligand, gave **11** in 95% yield after 18 h, although a kinetic study on one of the complexes revealed that the reaction was actually completed within one hour.[9, 20] In addition, using 0.5 mol% Ni(IPr)(PPh_3)Cl_2 (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) product **11** could be obtained in 39% yield in 30 minutes,[22] while a dinuclear nickel complex was reported to couple 4-chloroanisole with phenylmagnesium bromide in 91% yield in 12 h at the same catalyst loading.[12]

The best performing nickel NHC catalyst for the Kumada coupling of 4-fluoroanisole (**9-F**) with phenylmagnesium bromide reported to date consists of a 1:1 mixture of $Ni(acac)_2$ and a bulky imidazolium salt, leading to 58% conversion to **11** in 18 h with 5 mol% nickel.[24] Evidently, complex **8** is an extremely efficient catalyst, in terms of both reaction rate and selectivity.

The reactivity of complex **5b** has been reported for the Suzuki coupling of phenylboronic acid with 4-chloroanisole, amongst others.[13] This yielded 4-methoxybiphenyl in 92% yield after 18h, using 3 mol% of catalyst, 6 mol% of PPh_3 and stoichiometric amounts of K_3PO_4 as additional base, at 80 °C in toluene. Clearly, to obtain the desired coupling product the Kumada coupling is more efficient and economical.

5.2.5 Mechanistic considerations

As the present catalysts are the only ones described for the Kumada coupling using a ligand with an anionic pendant arm, it is believed that the relatively high rates in the catalytic runs must be due to the presence of these anionic side groups. The commonly accepted mechanism for the Kumada coupling consists of three consecutive steps: (1) oxidative addition of the aryl halide to a Ni(0) active species,



Scheme 5.2. Transition state proposed by Yoshikai *et al.*[26] (**A**) and proposed mechanism for the activation of the pre-catalyst and the transition state for carbon-halide bond activation for the system described in this chapter (**B** – **TS**).

(2) exchange of the halide on the nickel ion with the aryl group of the Grignard reagent (transmetalation) and (3) reductive elimination of the biaryl product, furnishing the coupling product and the starting Ni(0) species.[25] The Ni(0) species is believed to be obtained from the starting Ni(II) complex by two consecutive transmetalation steps, followed by a reductive elimination of biphenyl.

In the present case this implies that the two anionic N-donor moieties must be replaced by two phenyl groups, yielding a pendant anionic N-donor group, coordinated to the liberated $[MgCl]^+$ species (Scheme 5.2, **C**). These magnesium cations may then aid in the oxidative addition of the aryl halide, similar to a mechanism proposed by Yoshikai *et al.* (Scheme 5.2, **A**).[26] Based on a theoretical model, they designed a phosphane ligand with a benzylalcoholate pendant arm, which accelerated the Kumada coupling of aryl fluorides assumedly by a nickel/magnesium bimetallic cooperation. A transition state for the oxidative addition of the C–F bond was calculated, showing how a magnesium ion coordinated to the phenolato group assisted in the bond activation. The activation barrier was calculated to be only 6.4 kcal/mol instead of the 35.5 kcal/mol needed for the activation in the absence of the magnesium center. The high rate of our catalytic system may therefore also be explained by bimetallic cooperation, *i.e.* through a similar transition state (Scheme 5.1, **TS**).

5.3 Conclusions

A number of nickel complexes of chelating anionic ($C^\wedge N^-$) ligands have been prepared and characterized. Two new compounds are based on known amido-functionalized N-heterocyclic carbene ligands, two other nickel complexes are

obtained with novel anionic benzimidazole-functionalized carbene ligands. Unexpectedly, these compounds are highly active as homogeneous catalysts in the Kumada coupling of phenylmagnesium chloride with 4-chloroanisole. The highest rate and selectivity were obtained using a benzimidazole-functionalized NHC, yielding the desired product in quantitative yields with a TOF of 200 mol·(mol cat.)$^{-1}$·h^{-1}. Moreover, coupling of 4-fluoroanisole proceeded efficiently. The high rate of the reaction is explained by a possible nickel/magnesium bimetallic cooperation.

5.4 Experimental Section

General Procedures. All reactions were performed under an atmosphere of dry argon using standard Schlenk techniques. N-benzylbenzimidazole[27] and 2-chloro-N-phenylacetamide[14] were prepared according to literature procedures. All other chemicals were obtained from commercial sources and used as received. Solvents were reagent grade and used without further purification, except for THF and 1,4-dioxane, which were distilled from CaH_2 and stored on molecular sieves under argon. DMF was degassed prior to use. Nickel complex **5b** was prepared following a reported procedure.[13] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer and are referenced against tetramethylsilane. IR spectra were obtained on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. C,H,N determinations were performed on a Perkin-Elmer 2400 Series II analyzer. Electrospray mass spectra were recorded on a Finnigan TSQ-quantum instrument using an electrospray ionization technique (ESI-MS), using water/acetonitrile solutions. GC measurements were performed on a Varian CP-3800 gas chromatograph equipped with an autosampler. Retention times were compared to commercially obtained compounds. Diethyleneglycol-di-*n*-butylether was used as an internal standard.

1-Methyl-3-(N-phenylaminocarbonylmethyl)imidazolium chloride (1a). A mixture of 1.0 g 2-chloro-N-phenylacetamide (5.9 mmol) and 0.49 g N-methylimidazole (6.0 mmol) in 15 mL dry THF was stirred at 75 °C for 48 h. The colourless precipitate was isolated by filtration, washed with THF and diethyl ether and dried *in vacuo*. Recrystallization from methanol/diethyl ether afforded the pure compound. Yield: 1.46 g (98%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K) δ 11.29 (s, 1H, NH), 9.25 (s, 1H, NCHN), 7.79 (s, 1H, NCH), 7.74 (s, 1H, NCH), 7.66 (d, J = 8 Hz, 2H, Ar-H), 7.31 (t, J = 8 Hz, 2H, Ar-H), 7.06 (t, J = 8 Hz, 1H, Ar-H), 5.31 (s, 2H, CH_2), 3.91 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K) δ 163.7 (C=O), 138.5 (C_q), 137.8 (NCHN), 128.8 (Ar), 123.8 (NCH), 123.7 (Ar), 123.0 (NCH), 119.1 (Ar), 51.2 (CH_2), 35.8 (CH_3). IR (neat): 2979 (m), 1690 (s), 1553 (s), 1498 (m), 1444 (m), 1312 (m), 1254 (m), 1181 (s), 1108 (w), 942 (w), 784 (w), 752 (s), 695 (m), 622 (s) cm^{-1}. ESI-MS: *m*/*z* 216 ([M – Cl]$^+$, 100%). Anal. Calcd for $C_{12}H_{14}ClN_3O$: C, 57.26; H, 5.61; N, 16.69. Found: C, 57.58; H, 5.75; N, 17.08.

1-Benzyl-3-(N-phenylaminocarbonylmethyl)benzimidazolium chloride (2). This compound was synthesized following the procedure described for **1a**, starting from 1.70 g 2-chloro-N-phenylacetamide (10 mmol) and 2.08 g N-benzylbenzimidazole (10 mmol). Yield: 2.94 g (78%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 11.15 (s, 1H, NH), 10.05 (s, 1H, NCHN), 8.00 (m, 2H, Ar-H), 7.64-7.27 (m, 10H, Ar-H), 7.08 (m, 1H, Ar-H), 5.86 (s, 2H, CH_2), 5.63 (s, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 164.7 (C=O), 144.9 (NCHN), 139.5 (C_q), 135.1 (C_q), 133.1 (C_q), 131.6 (C_q), 130.3 (Ar), 130.2, (Ar), 130.1 (Ar), 129.5 (2 × Ar), 128.2 (Ar),

128.0 (Ar), 125.3 (Ar), 120.5 (Ar), 115.1 (Ar), 51.2 (CH_2), 50.4 (CH_2). IR (neat): 3023 (w), 2973 (w), 1685 (m), 1602 (m), 1560 (s), 1492 (m), 1447 (m), 1351 (m), 1311 (m), 1261 (m), 1188 (m), 949 (w), 753 (s), 692 (s), 640 (m) cm^{-1}. ESI-MS: *m*/*z* 341 ($[M - Cl]^+$, 100%). Anal. Calcd for $C_{22}H_{20}ClN_3O$: C, 69.93; H, 5.33; N, 11.12. Found: C, 69.77; H, 5.50; N, 11.04.

1-(Benzimidazol-2-ylmethyl)-3-benzylimidazolium chloride (3). A mixture of 2.37 g N-benzylimidazole (15.0 mmol) and 2.50 g 2-chloromethylbenzimidazole (15.0 mmol) in 20 mL dry 1,4-dioxane was stirred at 100 °C for 48 h. The reaction mixture was cooled and the off-white precipitate that had formed was collected by filtration, washed with THF and diethyl ether and dried *in vacuo*. The compound was further purified by recrystallization from MeOH/diethyl ether. Yield: 4.13 g (85%). ^{1}H NMR (300 MHz, D_2O, 300 K): δ 9.63 (s, 1H, NCHN), 7.97 (s, 1H, CH_{Im}), 7.90 (s, 1H, CH_{Im}), 7.58 (m, 2H, CH_{Bim}), 7.50-7.35 (m, 5H, Ar-H), 7.24 (m, 2H, CH_{Bim}), 5.85 (s, 2H, CH_2), 5.52 (s, 2H, CH_2). ^{13}C NMR (75 MHz, D_2O, 300 K): δ 147.8 (N=*C*(CH_2)N), 137.3 (NCHN), 134.7 (2 × C_q), 129.0 (Ar), 128.7 (Ar), 128.4 (Ar), 123.7 (?), 122.6 (?), 52.0 (CH_2), 46.2 (CH_2). IR (neat): 3050 (w), 2459 (w), 1559 (m) 1426 (m), 1331 (w), 1270 (w), 1218 (w), 1161 (m), 1012 (w), 839 (w), 797 (m), 741 (s), 700 (s), 635 (m), 618 (m) cm^{-1}. ESI-MS: *m*/*z* 289 ($[M - Cl]^+$, 100%). Anal. Calcd for $C_{18}H_{16}ClN_4 \cdot 2H_2O$: C, 60.08; H, 5.60; N, 15.57. Found: C, 59.95; H, 5.51; N, 15.55.

1-(Benzimidazol-2-ylmethyl)-3-benzylbenzimidazolium chloride (4). This ligand precursor was prepared following the procedure given for imidazolium salt **3**, starting from 2.08 g N-benzylbenzimidazole (10 mmol) and 1.67 g 2-chloromethylbenzimidazole (10 mmol) in 15 mL dry 1,4-dioxane. Yield: 1.95 g (52%). ^{1}H NMR (300 MHz, D_2O, 300 K): δ 9.79 (s, 1H, NCHN), 7.92 (m, 1H, Ar-H), 7.70 (m, 5H, Ar-H), 7.54 (m, 7H, Ar-H), 6.36 (s, 2H, CH_2), 5.80 (s, 2H, CH_2). The N*H* was not observed. ^{13}C NMR (75 MHz, D_2O, 300 K): δ 146.3 (N*C*(CH_2)N, 143.6 (NCHN), 133.7 (C_q), 133.3 (C_q), 132.2 (2 × C_q), 130.5 (Ar), 129.7 (Ar), 129.1 (Ar), 128.8 (Ar), 127.2 (Ar), 115.6 (Ar), 115.3 (2 × Ar), 113.7 (Ar), 52.2 (CH_2), 43.9 (CH_2). IR (neat): 2969 (w), 2485 (w), 1617 (w), 1555 (m), 1458 (w), 1428 (w), 1376 (w), 1220 (w), 1181 (m), 1027 (w), 880 (m), 754 (s), 710 (s), 619 (m), 597 (m) cm^{-1}. ESI-MS: *m*/*z* 339 ($[M - Cl]^+$, 100%). Anal. Calcd for $C_{22}H_{19}ClN_4 \cdot 1.8H_2O$: C, 64.88; H, 5.59; N, 13.76. Found: C, 64.86; H, 5.58; N, 13.95.

Bis(1-methyl-3-(N-phenylamidocarbonylmethyl)imidazol-2-ylidene)nickel(II) (5a). Based on the procedure given by Liao *et al.*,[13] a mixture of 0.38 g imidazolium salt **1a** (1.5 mmol), 97 mg dry $NiCl_2$ (0.75 mmol) and 0.62 g potassium carbonate (4.5 mmol) were heated in DMF at 130 °C for 16 h. After cooling, the yellow solution was filtered and the filtrate was evaporated to dryness *in vacuo*. The remaining solid was dissolved in dichloromethane and washed with water and brine. After drying with magnesium sulfate, the solvent was reduced in volume to 10 mL. Addition of diethyl ether yielded a bright yellow precipitate which was collected by filtration, washed with diethyl ether and dried *in vacuo*. The complex was purified by repeated recrystallization from methanol/hexane. Yield: 0.27 g (73%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K) δ 7.52 (d, *J* = 1.5 Hz, 2H, NCH), 7.25 (d, *J* = 7.5 Hz, 4H, Ar-H), 7.21 (d, *J* = 1.5 Hz, 2H, NCH), 6.91 (t, *J* = 7.5 Hz, 4H, Ar-H), 6.75 (t, *J* = 7.5 Hz, 2H, Ar-H), 5.71 (d, *J* = 14.5 Hz, 2H, CH_2), 4.31 (d, *J* = 14.5 Hz, 2H, CH_2), 3.13 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K) δ 166.8 (C_q), 165.5 (C_q), 147.2 (C_q), 126.5 (Ar), 125.6 (Ar), 122.6 (NCH), 122.2 (NCH), 120.8 (Ar), 56.8 (CH_2), 35.2 (CH_3). IR (neat): 3152 (w), 1601 (s), 1580 (s), 1558 (s), 1486 (m), 1445 (m), 1374 (s), 1296 (m), 1235 (m), 1075 (m), 754 (s), 693 (s), 534 (m), 502 (m) cm^{-1}. ESI-MS: *m*/*z* 487 ($[M + H]^+$, 100%), 216 ($[ligand]^+$). Anal. Calcd for $C_{24}H_{24}N_6NiO_2 \cdot H_2O$: C, 57.06; H, 5.19; N, 16.63. Found: C, 56.80; H, 5.51; N, 16.39.

Bis(1-benzyl-3-(N-phenylamidocarbonylmethyl)benzimidazol-2-ylidene)nickel(II) (6). This compound was synthesized according to the procedure given for **5a**, starting from 1.13 g benzimidazolium salt **2** (3.0 mmol), 1.23 g potassium carbonate (9.0 mmol) and 0.19 g dry $NiCl_2$ (1.5 mmol) in 40 mL DMF. The complex was purified by repeated recrystallization from dichloromethane/diethyl ether. Yield: 0.78 g (70%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K) δ 7.94 (d, *J* = 8 Hz, 2H, Ar-H), 7.53 (d, *J* = 8 Hz, 2H, Ar-H), 7.40 (t, *J* = 8 Hz, 2H, Ar-H), 7.29 (t, *J* = 8 Hz, 2H, Ar-H), 7.21 (m, 6H, Ar-H), 6.95-6.70 (m, 14H, Ar-H), 5.61 (m, 4H, CH_2), 4.85 (d, *J* = 16 Hz, 2H, CH_2), 4.58 (d, *J* = 16 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K) δ 179.5 (Ni-C), 166.4 (C=O), 146.4 (C_q), 136.2 (C_q), 134.5 (C_q), 133.8 (C_q), 128.7 (Ar), 127.7 (Ar), 126.2 (Ar), 126.1 (Ar), 125.7 (Ar), 123.8 (Ar), 123.4 (Ar), 121.2 (Ar), 111.4 (Ar), 110.6 (Ar), 53.9 (CH_2), 49.8 (CH_2). IR (neat): 3131 (w), 1603 (s), 1581 (s), 1570 (s), 1486 (m), 1446 (s), 1362 (s), 1220 (m), 1078 (m), 1026 (m), 970 (w), 754 (m), 739 (s), 722 (m), 693 (s) cm^{-1}. ESI-MS: *m*/*z* 739 ([M + H]$^+$, 100%). Anal. Calcd for $C_{44}H_{36}N_6NiO_2 \cdot 1.5H_2O$: C, 68.94; H, 5.13; N, 10.96. Found: C, 69.09; H, 5.08; N, 10.94.

Bis(1-(benzimidazolato-2-ylmethyl)-3-benzylimidazol-2-ylidene)nickel(II) (7). This complex was obtained following the procedure given for complex **5a**, starting from 0.97 g imidazolium salt **3** (3.0 mmol), 1.23 g potassium carbonate (9.0 mmol) and 0.19 g dry $NiCl_2$ (1.5 mmol) in 40 mL DMF. The complex was purified by recrystallization from dichloromethane/diethyl ether. Yield: 0.74 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.68 (d, *J* = 8 Hz, 2H, Ar-H), 7.45-7.05 (m, 12H, Ar-H), 6.93 (t, *J* = 8 Hz, 2H, Ar-H), 6.78 (m, 3H, Ar-H), 6.42 (m, 3H, Ar-H), 5.66 (d, *J* = 15 Hz, 2H, CH_2), 5.19 (d, *J* = 15 Hz, 2H, CH_2), 3.93 (d, *J* = 16 Hz, 2H, CH_2), 3.80 (d, *J* = 16 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 171.2 (Ni-C), 155.5 (C_q), 146.2 (C_q), 144.1 (C_q), 136.3 (C_q), 128.8 (Ar), 127.9 (Ar), 127.3 (Ar), 121.6 (Ar), 121.1 (Ar), 120.2 (Im-C), 120.0 (Im-C), 118.8 (Ar), 113.4 (Ar), 52.5 (CH_2), 50.7 (CH_2). IR (neat): 3060 (w), 1605 (w), 1446 (m), 1393 (m), 1304 (w), 1270 (m), 1338 (w), 1158 (w), 857 (w), 741 (s), 726 (s), 702 (s) cm^{-1}. ESI-MS: *m*/*z* 633 ([M + H]$^+$, 100%). Anal. Calcd for $C_{36}H_{30}N_8Ni \cdot H_2O$: C, 66.38; H, 4.95; N, 17.20. Found: C, 66.43; H, 5.23; N, 17.43.

Bis(1-(benzimidazolato-2-ylmethyl)-3-benzylbenzimidazol-2-ylidene)nickel(II) (8). This compound was synthesized following the procedure given for complex **5a**, starting from 1.13 g benzimidazolium salt **4** (3.0 mmol), 0.19 g dry $NiCl_2$ (1.5 mmol), 1.23 g potassium carbonate (9.0 mmol) in 40 mL DMF. Recrystallization from chloroform/diethyl ether yielded the pure compound. Yield: 0.67 g (61%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.55 (d, 2H, *J* = 8 Hz, Ar-H_{Bim}), 7.43 (d, 2H, *J* = 8 Hz, Ar-H_{Bim}-), 7.29 (t, 2H, *J* = 8 Hz, Ar-H_{Bim}), 7.25 – 7.05 (m, 14H, Ar-H), 6.75 (dt, 2H, *J* = 1 Hz, *J* = 8 Hz, Ar-H_{Bim}-), 6.42 (dt, 2H, *J* = 1 Hz, *J* = 8 Hz, Ar-H_{Bim}-), 6.08 (d, 2H, *J* = 8 Hz, Ar-H_{Bim}-), 5.92 (d, 2H, *J* = 14 Hz, NCH_2CN_2), 5.81 (d, 2H, *J* = 14 Hz, NCH_2CN_2), 5.28 (d, 2H, *J* = 16 Hz, CH_2Ph), 4.79 (d, 2H, *J* = 16 Hz, CH_2Ph). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 181.2 (Ni-C), 153.5 (C_q NiN*C*=N(CH_2)), 143.6 (C_q benzyl), 134.1 (3 × C_q benzimidazole), 134.0 (C_q benzimidazole), 129.0 (Ar benzyl), 128.4 (Ar), 125.7 (Ar benzyl), 124.4 (Ar), 123.8 (Ar), 120.1 (Ar), 119.8 (Ar), 117.6 (Ar), 114.6 (Ar), 110.5 (2 × Ar), 50.7 (CH_2), 47.5 (CH_2). IR (neat): 3059 (w), 1606 (w), 1476 (w), 1446 (m), 1394 (m), 1340 (w), 1310 (w), 1269 (m), 1211 (w), 1182 (w), 735 (s), 702 (m) cm^{-1}. ESI-MS: *m*/*z* 733 ([M + H]$^+$, 100%). Anal. Calcd for $C_{44}H_{34}N_8Ni \cdot 0.25CHCl_3$: C, 69.62; H, 4.52; N, 14.68. Found: C, 69.44; H, 4.86; N, 15.00.

General procedure for the Kumada coupling. At room temperature, 0.03 mmol nickel complex was dissolved/suspended in 1.0 mL THF, followed by the addition of 1.0 mmol of the 4-haloanisole. The reaction was started with the addition of 1.5 mmol phenylmagnesium

chloride (25 wt% in THF, 0.78 mL) and monitored by taking samples at regular intervals until GC analysis showed full consumption of the 4-haloanisole. All catalytic reactions were performed in duplicate and were found to give consistent results. To isolate the desired coupling product, water was added to the reaction mixture, followed by extraction into ethyl acetate (3 × 20 mL). The organic fractions were combined, dried with magnesium sulfate and evaporated to dryness. Purification by column chromatography on silica gel (95:5 hexane:dichloromethane) yielded 4-methoxybiphenyl as a colorless solid. ^{1}H NMR and ^{13}C NMR spectra were in agreement with the proposed structure,[11] and the GC retention time corresponded to that of a commercial reference sample.

X-ray crystal structure determinations. X-ray reflections were measured with Mo-Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer with rotating anode at a temperature of 150 K. The intensities were integrated using HKL2000.[28] Absorption correction, scaling and merging was performed with SORTAV.[29] The structures were solved with Direct Methods (program SIR-97[30] for **5a** and **6**, program SHELXS-97[31] for **8**). Refinement was performed with SHELXL-97[31] against F^2 of all reflections. Non hydrogen

Table 5.4. Details of the X-ray crystal structure determinations

	5a	**6**	**8**
formula	$C_{24}H_{24}N_6NiO_2 \cdot 2CH_3OH \cdot 0.5H_2O$	$C_{44}H_{36}N_6NiO_2$ + disordered solvent	$C_{44}H_{34}N_8Ni$ + disordered solvent
FW	560.29	739.50 [a]	733.50 [a]
Crystal colour	Yellow	yellow	yellow
crystal size [mm^3]	0.60x0.24x0.09	0.30x0.30x0.20	0.30x0.30x0.20
Crystal system	Monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	20.7321(3)	11.3697(2)	12.5841(1)
b [Å]	8.5908(1)	16.9361(4)	13.4533(2)
c [Å]	33.5771(6)	24.0007(6)	15.7310(2)
α [°]	-	-	109.7758(8)
β [°]	117.8263(8)	115.0097(13)	103.2347(6)
γ [°]	-	-	95.7404(5)
V [Å^3]	5288.74(14)	4188.20(16)	2393.36(5)
Z	8	4	2
D_x [g/cm^3]	1.407	1.173 [a]	1.018 [a]
$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.65	0.60	0.65
refl. meas./unique	41023 / 11971	33596 / 7579	44462 / 10861
μ [mm^{-1}]	0.78	0.50 [a]	0.44 [a]
abs. corr.	multi-scan	multi-scan	multi-scan
abs. corr. range	0.84-0.94	0.75-0.90	0.76-0.92
param./restraints	684 / 0	478 / 0	481 / 0
R1/wR2 [I>2σ(I)]	0.0420 / 0.1007	0.0608 / 0.1601	0.0404 / 0.1009
R1/wR2 [all refl.]	0.0661 / 0.1144	0.0893 / 0.1730	0.0534 / 0.1050
R(int)	0.0549	0.0672	0.0514
S	1.065	1.059	1.061
Res. density [e/Å^3]	-0.43 / 0.90	-0.43 / 1.03	-0.39 / 0.33

[a] Derived values do not contain the contribution of the disordered solvent.

atoms were refined with anisotropic displacement parameters. In **5a** all hydrogen atoms were located in difference Fourier maps. O-H hydrogen atoms were kept fixed at their located position; C-H hydrogen atoms were refined with a riding model. In **6** and **8**, all hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[32] Further details are given in Table 5.4.

Crystal structures **6** and **8** contain large solvent-accessible voids (880 Å^3/unit cell in **6**, 852 Å^3/unit cell in **8**) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of PLATON,[32] resulting in 199 electrons/unit cell for **6** and 367 electrons/unit cell for **8**.

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