



## Nickel N-heterocyclic carbene complexes in homogeneous catalysis

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# Chapter 4

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## Synthesis of novel chelating benzimidazole-based carbenes and their nickel(II) complexes; activity in the Kumada coupling reaction<sup>†</sup>

**Abstract.** Nickel(II) halide complexes of novel chelating bidentate benzimidazole-based *N*-heterocyclic carbenes have been prepared from  $\text{Ni}(\text{OAc})_2$  and bisbenzimidazolium salts. Single-crystal X-ray structure determination on four complexes revealed a *cis*-geometry on a square-planar nickel center. The complexes are active catalysts for the Kumada coupling of 4-chloroanisole and 4-bromoanisole with phenylmagnesium chloride. The most active catalyst gives a complete conversion of 4-bromoanisole within 75 minutes with a selectivity to 4-methoxybiphenyl of 82% and a complete conversion of 4-chloroanisole in less than 14 hours with a selectivity to 4-methoxybiphenyl of 99%.

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<sup>†</sup> Based on J. Berding, M. Lutz, A. L. Spek, E. Bouwman, *Organometallics*, **2009**, *28*, 1845.

## 4.1 Introduction

Since the first isolation of a stable, free N-heterocyclic carbene (NHC) by Arduengo in 1991,<sup>1</sup> complexes with NHC ligands have found application in a wide variety of homogeneous catalysts. The strong  $\sigma$ -donating properties of carbenes have often been compared to those of phosphane ligands, which are known to stabilize various oxidation states of a transition metal in a catalytic cycle. Ligand dissociation, a known occurrence in phosphane complexes, is less likely to take place when NHCs are used instead.<sup>2, 3</sup> Some excellent reviews have been published on the development and use of NHCs.<sup>4-6</sup> Research has been focused mainly on replacing phosphane ligands in known catalytic systems; well known is the second generation Grubbs' catalyst with one NHC and one phosphane ligand, which showed a large improvement in reactivity and stability compared to the first-generation catalyst bearing two phosphane ligands.<sup>7</sup> Recently, in our group, nickel complexes with bidentate phosphane ligands were found to be active homogeneous catalysts in alkene hydrogenation.<sup>8, 9</sup> Inspired by this discovery, it was decided to investigate the catalytic activity of nickel complexes with bidentate carbene ligands.

Carbon-carbon bond formation is one of the most important transition-metal catalyzed reactions in organic synthesis. Cross-coupling reactions between aryl halides or aryl triflates and aryl-M (M = B(OR)<sub>2</sub>, SnR<sub>3</sub>, SiR<sub>3</sub>, MgX) leading to the formation of biaryl derivatives have been investigated extensively.<sup>10-12</sup> Palladium often yields the most efficient catalyst, showing good activity in a variety of C–C coupling reactions. Some nickel complexes are known to be efficient C–C coupling catalysts as well, both with monodentate and chelating phosphane ligands.<sup>13-17</sup> However, only a few nickel complexes with N-heterocyclic carbene ligands have been reported as catalysts in aryl-aryl coupling reactions.<sup>18-21</sup> It was decided to focus on the coupling of Grignard reagents with aryl halides, a reaction that was reported independently by both Kumada and Corriu in 1972.<sup>13, 22</sup> Aryl-aryl coupling reactions utilizing aryl boronic acids, stannanes and silicon and zinc derivatives have a better functional group tolerance and have been studied in more detail. However, often their starting compounds are less reactive and have to be prepared from the Grignard or organolithium precursor. The advantage of the Kumada reaction is therefore the elimination of one synthetic step. Two systems based on nickel compounds in combination with imidazolium salts have been reported to catalyze the Kumada reaction. The nickel NHC complex is presumed to be formed *in situ*;<sup>23-25</sup> other systems make use of preformed nickel complexes.<sup>26-29</sup>

The study described in this chapter focused on nickel complexes of the type (bisNHC)NiX<sub>2</sub>, in which bisNHC is a *chelating* bidentate bis(imidazol-2-ylidene) ligand. In literature a number of attempts to obtain this type of complex with two halide anions has been reported to be unsuccessful, leading only to intractable reaction mixtures,<sup>30</sup> or to homoleptic [(bisNHC)<sub>2</sub>Ni]<sup>2+</sup> complexes.<sup>31, 32</sup> A successful attempt by Baker *et al.* resulted in the synthesis of a nickel complex (**I**) derived from an imidazolium-linked *ortho*-cyclophane (Figure 4.1).<sup>33</sup> Douthwaite *et al.* were able to prepare two types of bisNHC nickel complexes; one bearing an additional PMe<sub>3</sub> ligand,<sup>34</sup> the other a bisNHC nickel

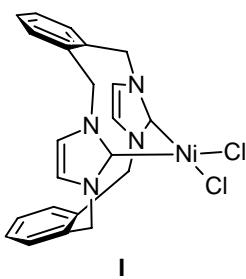


Figure 4.1. *cis*-(BisNHC) nickel complex prepared by Baker *et al.*<sup>33</sup>

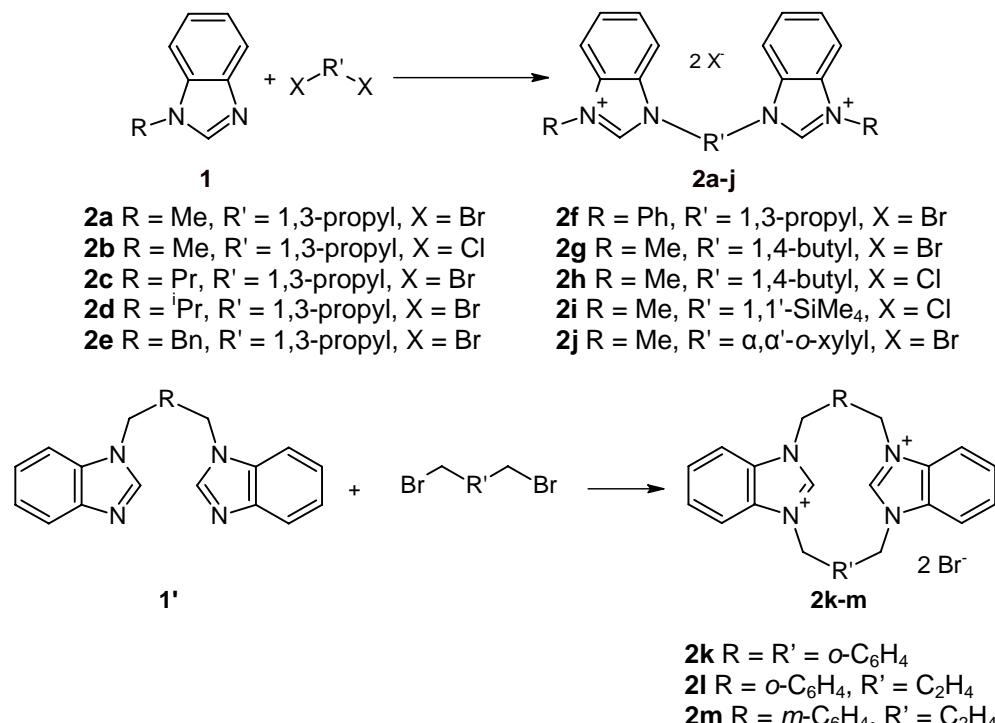
complex with two methyl ligands.<sup>30</sup> One bisNHC dihalido complex has been reported with a very long bridging moiety leading to a *trans* geometry.<sup>35</sup>

Recently, Hahn *et al.*, who described the first benzimidazole-based free carbene in 1999,<sup>36</sup> reported the successful synthesis of a dihalido nickel complex bearing two monodentate bis(benzimidazol-2-ylidene) ligands.<sup>37</sup> In this chapter the synthesis and characterization of new dihalido nickel complexes of novel chelating bisNHC ligands are described. These compounds are efficient catalysts for the Kumada coupling reaction of aryl chlorides and bromides with aryl magnesium chloride under mild conditions.

## 4.2 Results and Discussion

### 4.2.1 Preparation of Alkyl-Bridged Bisbenzimidazolium Salts

Bisbenzimidazolium salts are relatively unknown, compared to the widely used alkyl-bridged bisimidazolium salts. Both may be obtained by quaternization of an



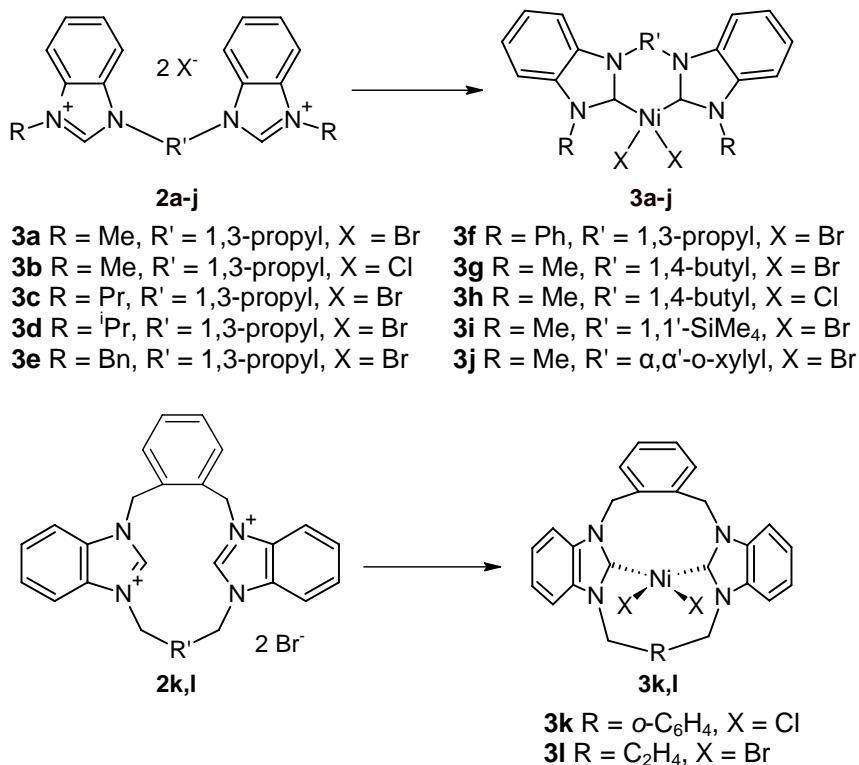
Scheme 4.1. Bisbenzimidazolium salts described in this chapter.

N-substituted (benz)imidazole with a dihaloalkane,<sup>38</sup> or by reacting a bridged di(benz)imidazole with two equivalents of an alkyl halide.<sup>39</sup> In this study dihaloalkanes were reacted with an excess of N-substituted benzimidazoles **1** in hot 1,4-dioxane to furnish the bridged bisbenzimidazolium salts **2a-j** shown in Scheme 4.1. 1,4-Dioxane was chosen as a solvent instead of the more commonly used THF, because it can be used at higher temperatures, thus reducing reaction times. The white bisbenzimidazolium salts **2a-j** were obtained in good yields and high purity. Cyclic salts **2k** and **2l** were prepared according to literature procedures by reaction of 1,1'-( $\alpha,\alpha'$ -o-xyxyl)dibenzimidazole with  $\alpha,\alpha'$ -dibromo-*o*-xylene, or 1,4-dibromobutane, respectively.<sup>39, 40</sup> Similarly, **2m** was obtained by treating 1,1'-( $\alpha,\alpha'$ -*m*-xylyl)dibenzimidazole with excess 1,4-dibromobutane under high dilution conditions.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the bisbenzimidazolium salts in DMSO-*d*<sub>6</sub> show the characteristic resonances of the benzimidazolium NCHN proton and carbon downfield at around 10 and 140 ppm, respectively.<sup>41</sup> The iodide salts of **2a**,<sup>42</sup> **2g,h,j**,<sup>39</sup> and the chloride salt of **2e**,<sup>43</sup> are known in literature and our findings are consistent with the reported NMR data.

#### 4.2.2 Preparation of Nickel Complexes.

McGuinness *et al.*<sup>44</sup> developed a method in which imidazolium iodides bearing small N-substituents were melted and reacted directly with Ni(OAc)<sub>2</sub> in *vacuo* to yield the corresponding Ni(NHC)<sub>2</sub>I<sub>2</sub> complexes. The melting points of the larger azolium salts,



Scheme 4.2. Nickel(II) bisNHC complexes prepared in this study.

however, are too high for this procedure, resulting in decomposition. This problem was overcome for the benzimidazolium salts by adding another non-reactive, low-melting salt (tetrabutylammonium iodide or bromide) to the reaction mixture as an ionic liquid solvent.<sup>37</sup> This allowed the use of lower reaction temperatures (120 °C) and afforded the nickel complexes in good yield. The latter method has been used in this study to obtain dihalidonickel complexes with chelating bisbenzimidazol-2-ylidene ligands (**3a-j,3l**, Scheme 4.2).

Nickel complexes **3a-j** and **3l** were obtained as yellow solids after trituration of the reaction mixture with water to remove the tetrabutylammonium salt and unreacted starting material. Further purification was accomplished by dissolving the crude product in dichloromethane and washing with water and brine. Unfortunately, treatment of **2m** with  $\text{Ni}(\text{OAc})_2$  under the same conditions did not yield any isolable complex. Compound **3h** is soluble in water and work-up was performed omitting the filtration after trituration with water. All complexes are stable towards air and moisture and are soluble in dichloromethane, acetonitrile and DMSO, sparingly soluble in THF and insoluble in diethyl ether and hexane. In the synthesis of **3g** and **3h** a more diluted reaction mixture was used to avoid the formation of polynuclear species. The reaction of **2i** with nickel acetate in tetrabutylammonium chloride did not give a stable isolable product. Alternatively, it was reacted in tetrabutylammonium bromide with potassium bromide added to ensure the presence of a large excess of bromide anions. From this mixture the nickel bromide complex **3i** could be obtained. Treatment of cyclic bisbenzimidazolium salt **2k** with  $\text{KPF}_6$  in methanol furnished the corresponding hexafluoridophosphate salt which was subsequently reacted with  $\text{NiCl}_2$  and  $\text{NaOAc}$  in DMF, following the synthetic procedure reported by Baker *et al.* for cyclophane-based nickel complex **I**.<sup>33</sup> This yielded the corresponding dichloridonickel complex **3k** as a yellow solid.

Initially, a satisfactory elemental analysis could not be obtained for a number of dibromide complexes. Potentiometric titration of a solution of the analytical samples of two of these complexes with silver nitrate revealed that during the washing with brine the bromide anions were replaced by chlorides. The elemental analyses were consistent with the Cl : Br ratios thus found. Therefore, instead of the final washing with brine, the dichloromethane solutions of the bromide complexes were washed with a sodium bromide solution. The elemental analyses of the complexes thus obtained were consistent with a dibromido formulation. The elemental analyses of complexes obtained before the extraction were unsatisfactory due to the presence of varying amounts of tetrabutylammonium salts.

The square-planar low-spin nickel complexes are diamagnetic and give rise to clear <sup>1</sup>H and <sup>13</sup>C NMR spectra. With the exception of shifts of the signals of the bridging moieties, there are only minor changes in the <sup>1</sup>H NMR spectra compared to the benzimidazolium salts. The benzimidazolium NCHN is absent in the <sup>1</sup>H NMR spectra of the complexes, confirming carbene generation. A representative example, the <sup>1</sup>H NMR spectra of bisbenzimidazolium salt **2a** and nickel complex **3a**, is depicted in Figure 4.2. Due to conformational constraints and possibly interaction with the nickel center the

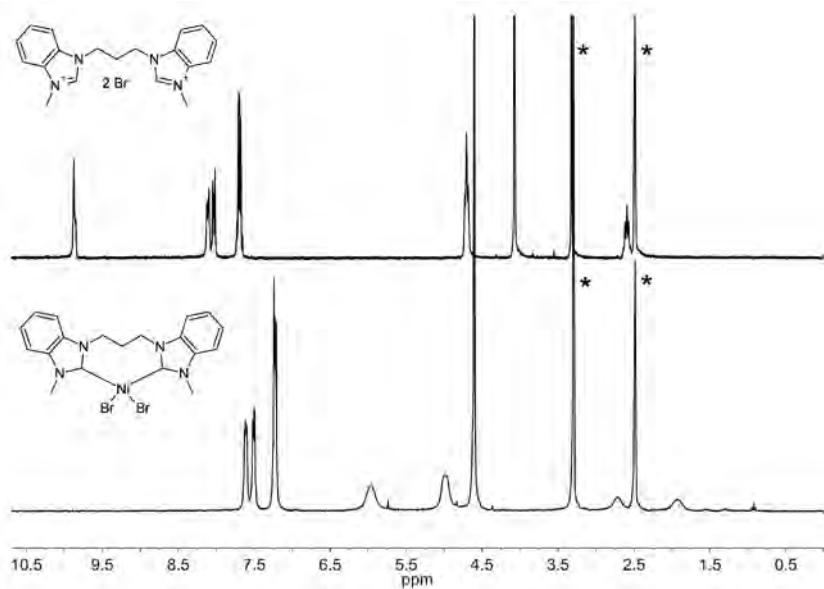


Figure 4.2.  $^1\text{H}$  NMR spectra of bisbenzimidazolium salt **2a** and complex **3a**. Peaks marked with (\*) are solvent signals.

resonances of the bridging moieties are split over a range up to 2.1 ppm for the o-xylyl bridged complex **3j**. The splitting of the resonances of bridges of the cyclic bisNHC ligands are even larger; for **3k** the splitting is about 2.6 ppm (as was observed for **I**)<sup>33</sup>, while for **3l** this is also 2.1 ppm. As an example, the  $^1\text{H}$  COSY NMR spectrum of **3l**, which was used to assign the resonances of the bridges, is shown in Figure 4.3. Unfortunately, due to peak broadening the carbene–C resonance could not be observed in the  $^{13}\text{C}$  NMR spectra for all complexes.

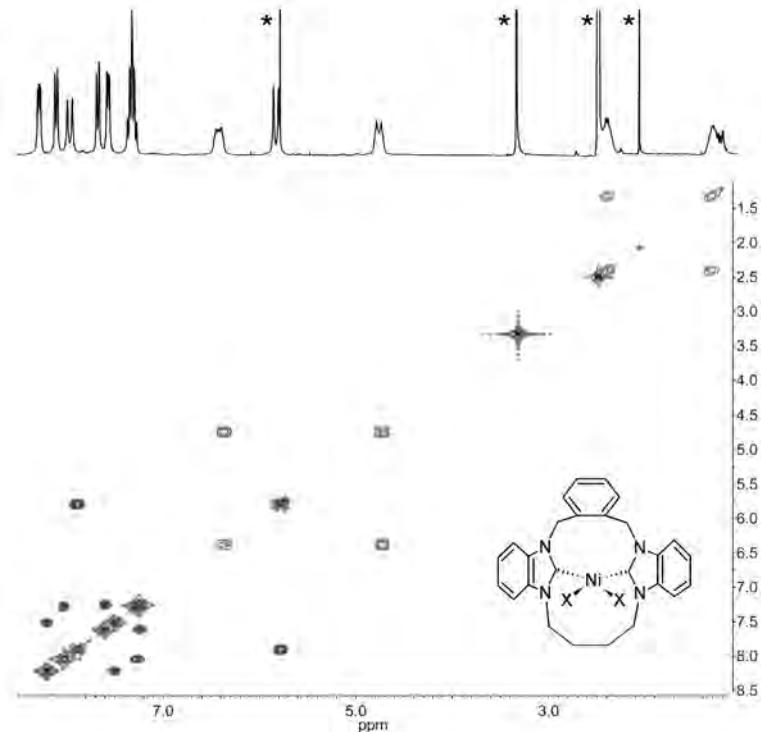


Figure 4.3.  $^1\text{H}$  COSY NMR spectrum of complex **3l**. Peaks marked with (\*) are solvent signals.

#### 4.2.3 Description of the structures

Dark yellow single crystals of **3a**, **3e**, **3g** and **3i** were obtained from dichloromethane/acetonitrile or dichloromethane/diethyl ether solutions by slow evaporation, and their molecular structures were determined by X-ray diffraction. Molecular plots of **3a**, **3e**, **3g** and **3i** are shown in Figure 4.4 and selected bond distances and angles are collected in Table 4.1. All complexes show a *cis*-geometry around a slightly distorted square-planar nickel center, with the two bromide ions twisted out of the  $C_2Ni$  plane by 5.3(3) to 9.9(2) degrees. The coordination bond lengths in the four complexes are rather similar and the Ni-C distances are only slightly shorter than those reported for the related *trans*-[Ni(NHC)<sub>2</sub>Br<sub>2</sub>] (NHC = 1,3-dipropylbenzimidazol-2-ylidene).<sup>37</sup> The C12–Ni–C22 bite angle changes slightly upon lengthening of the bridging moiety, from 85.8(2) $^{\circ}$  for the propyl bridge to 91.0(2) $^{\circ}$  for the butyl bridge. Compared to the chelating phosphanes, where every additional carbon in the chain leads to an increase in bite angle of 8 – 10 $^{\circ}$ , this is a relatively small difference.<sup>34</sup> This smaller effect in the bite angle is due to the angle at which the benzimidazole rings are twisted relative to the coordination plane (Table 4.1). On average, the ligands with a longer bridge have their benzimidazole rings closer to a plane perpendicular to the plane of coordination, as was observed in a palladium analogue,<sup>45</sup> and a rhodium di(imidazol-2-ylidene) complex with

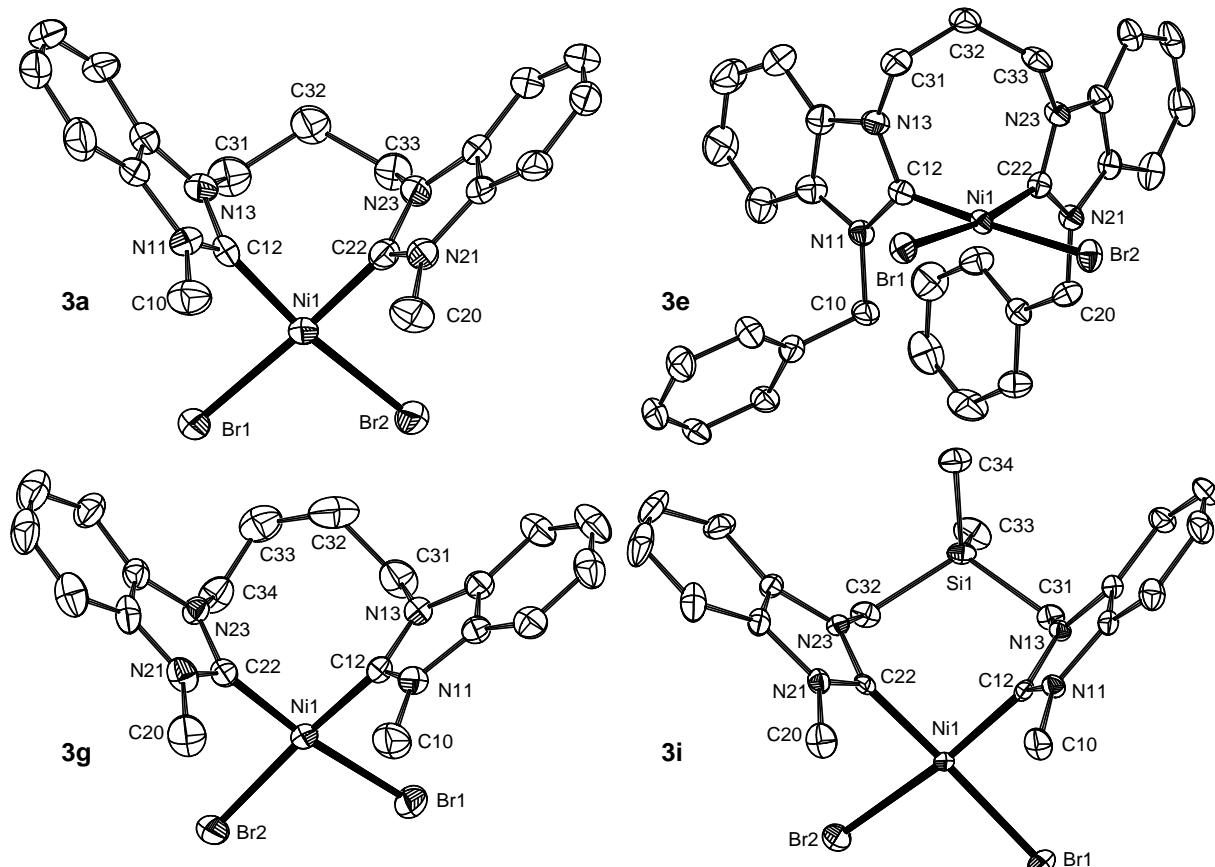


Figure 4.4. Displacement ellipsoid plots of **3a**, **3e**, **3g** and **3i** at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 4.1. Selected Bond Lengths (Å) and Angles (deg) for complexes **3a**, **3e**, **3g** and **3i**

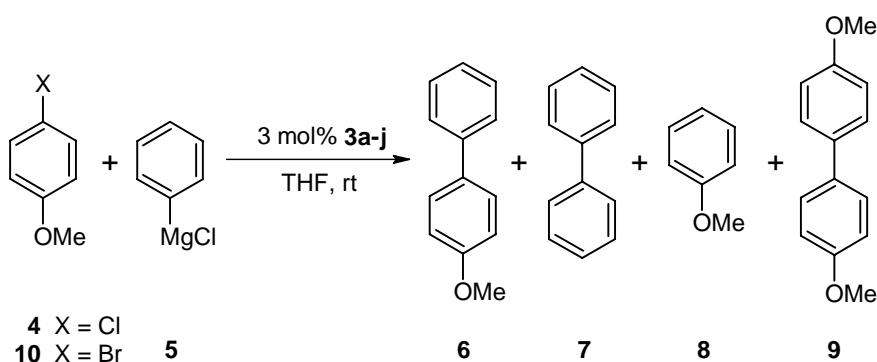
	<b>3a</b>	<b>3e</b>	<b>3g</b>	<b>3i</b>
Ni–Br1	2.3545(10)	2.3400(9)	2.3491(8)	2.3383(4)
Ni–Br2	2.3568(10)	2.3447(10)	2.3384(8)	2.3516(4)
Ni–C12	1.859(6)	1.863(6)	1.867(5)	1.872(2)
Ni–C22	1.859(6)	1.861(6)	1.860(5)	1.865(2)
N11–C12	1.369(8)	1.346(8)	1.350(6)	1.353(3)
N13–C12	1.343(8)	1.367(8)	1.346(6)	1.355(3)
N21–C22	1.368(8)	1.368(8)	1.359(6)	1.354(3)
N23–C22	1.341(8)	1.345(8)	1.364(6)	1.354(3)
Br1–Ni–Br2	95.95(4)	95.09(4)	94.26(3)	95.039(14)
C12–Ni–C22	85.8(2)	85.9(3)	91.0(2)	89.51(10)
C12–Ni–Br1	90.27(17)	90.50(17)	85.32(14)	90.47(7)
C22–Ni–Br2	88.20(18)	88.54(18)	90.28(14)	85.37(7)
N11–C12–N13	106.6(5)	106.9(5)	106.6(4)	106.5(2)
N21–C22–N23	106.9(5)	106.4(5)	105.5(4)	106.9(2)
NiC <sub>2</sub> / carbene dihedral angle <sup>a</sup>	84.4(4) 83.5(5)	81.7(4) 84.5(3)	88.1(3) 86.8(3)	85.80(14) 85.82(15)
T <sub>d</sub> twist <sup>b</sup>	5.3(3)	8.8(3)	9.9(2)	6.76(11)

<sup>a</sup> NiC<sub>2</sub> / Carbene dihedral angle = angle between LS planes; one through the imidazole ring; one through Ni–C12–C22; <sup>b</sup> T<sub>d</sub> twist = angle between LS planes through Br1–Ni–Br2 and C12–Ni–C22.

bridges of varying lengths.<sup>46</sup>

Although a plane of symmetry is present in the free ligands, in all cases the complexes crystallized asymmetrically due to packing effects. The benzimidazole moieties are twisted out of the plane perpendicular to the C<sub>2</sub>Ni plane by a few degrees, as mentioned before. These are, however, twisted to a different degree, leading to two values for the NiC<sub>2</sub> / carbene dihedral angle as shown in Table 4.1.

In the crystal structure of complex **3g** the C<sub>4</sub> bridge is asymmetric, as exemplified by the difference in torsion angles around the C31–C32 (eclipsed, -124.0(5)<sup>o</sup>) and the C34–C33 (staggered, 51.6(7)<sup>o</sup>) bonds. This leads to a weak anagostic interaction between the nickel and one of the NCH<sub>2</sub> hydrogens (*d*(H–M) = 2.65 Å,  $\theta$ (C–H–M) = 117<sup>o</sup>).<sup>47</sup> A similar asymmetry is also observed in the structure of a related palladium complex (1,1'-dimethyl-3,3'-(1,4-butanediyl)diimidazol-2,2'-diylidene)palladium(II) chloride.<sup>48</sup> The bridges in **3a**, **3e** and **3i** show staggered conformations along their C31–C32, C33–C32 and C31–Si1, C31–Si1 bonds, as expected.



Scheme 4.3. Nickel-catalyzed Kumada coupling of 4-haloanisole and phenylmagnesium chloride.

#### 4.2.4 Catalytic studies

Complexes **3a-j** were tested as catalysts in the coupling of 4-chloro- and 4-bromoanisole with phenylmagnesium chloride (Scheme 4.3). Apart from the desired product 4-methoxybiphenyl (**6**), varying amounts of biphenyl (**7**), anisole (**8**) and bisanisole (**9**) are observed in the reaction mixtures. The activity for the different catalysts – given as the time needed to consume all starting aryl halide – and the yields (in mmol) of the various products are summarized in Table 4.2 and Table 4.3. The total amount of product varies, due to the excess of Grignard reagent used and the fact that unreacted Grignard reagent could not be detected by GC analysis. The total amount of **6** and **8** plus twice the amount of **9** should be equal to 1 mmol; the amount of **7** should not exceed half the amount of Grignard reagent that was not used in the formation of **6**, which is equal to  $0.5 \times (1.5 \text{ mmol} - \text{the amount of } \mathbf{6})$ . Within experimental error, both requirements are met in all catalytic runs. As an example, a plot of the evolution in time of the substrate and products in a typical catalytic experiment starting from 4-bromoanisole and using **3j** as catalyst is shown in Figure 4.5. In this case the reaction starts immediately, whereas with some of the catalysts a short induction time is observed. The amounts of the byproducts

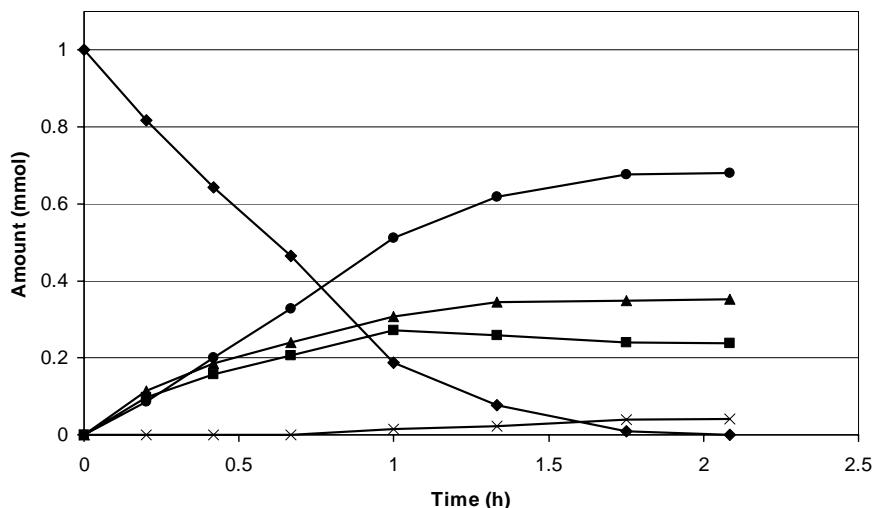


Figure 4.5. Evolution of the products in time of a typical catalytic experiment (Table 4.3, entry 3). (♦) 4-bromoanisole; (●) 4-methoxybiphenyl; (▲) biphenyl; (■) anisole; (×) bisanisole.

Table 4.2. Nickel-catalyzed Kumada cross-coupling of 4-chloroanisole and phenylmagnesium chloride at room temperature.<sup>a</sup>

Entry	Complex	Time to completion (h)	Yield (10 <sup>-2</sup> mmol) <sup>b</sup>			
			6	7	8	9
1	<b>3a</b>	37	85	18	3	6
2	<b>3b</b>	35	83	16	3	7
3	<b>3c</b>	18	88	13	6	3
4	<b>3d</b>	15	82	25	1	7
5	<b>3e</b>	<14	99 (93)	4	0	0
6	<b>3f</b>	18	75	37	13	8
7	<b>3g</b>	16	99 (91)	7	0	0
8	<b>3h</b>	18	99	8	0	0
9	<b>3i</b>	25	92	18	3	3
10	<b>3j</b>	15	80	27	6	7
11	Ni(acac) <sub>2</sub> <sup>+</sup> iPr-HCl <sup>c</sup>	18	71	16	1	9
12	(C <sup>3</sup> P)NiBr <sub>3</sub> <sup>d</sup>	18	95	19	0	1

<sup>a</sup> Reaction conditions: 1.0 mmol 4-chloroanisole, 1.5 mmol phenylmagnesium chloride (25 w% in THF), 0.03 mmol catalyst, 1 mL THF, room temperature; <sup>b</sup> GC yields, average of two runs. Isolated yield in parentheses; <sup>c</sup> 81% conversion after 18 h, ref. 23; <sup>d</sup> 96% conversion after 18 h, ref. 24.

biphenyl and anisole increase in the first hour, but then stabilize to the final composition, while the conversion of the substrates to the desired product continues. Bisanisole is not detected in the first 45 minutes of the reaction.

All the new complexes **3a-j** are able to catalyze the coupling of 4-chloroanisole with phenylmagnesium chloride (Table 4.2); however, the rate and the selectivity depend to a large extent on the complex used. Full conversion is achieved in less than 14 hours (entry 5) up to 37 hours (entry 2), furnishing the desired product in 75% (entry 6) to nearly quantitative yields (entries 5, 7 and 8). The halide anion present in the starting nickel complex does not have an effect on the rate and the selectivity of the reaction, as **3a** and **3b** (entries 1 and 2) give the same results, within experimental error, as do **3g** and **3h** (entries 7 and 8). The various N-substituents of the ligands do have an effect on the rate and selectivity of the catalysts (entries 1 and 3-6). The rate of the reaction decreases in the order Bn > iPr > Pr = Ph > Me. The selectivity towards the desired product 4-methoxybiphenyl decreases in the order Bn > Pr > Me ≥ iPr > Ph. The influence of the bridging moiety can be established from a comparison of the results of complexes **3a,h-j** (entries 1 and 7-10) as these complexes only differ in the bridging part. For this series of complexes the time necessary to complete the reaction increases in the order o-Xy < Bu < Si < Pr. The selectivity towards 4-methoxybiphenyl decreases in the order Bu > Si > Pr > o-Xy. The most efficient catalyst for the coupling of 4-chloroanisole and phenylmagnesium chloride thus found in this study is complex **3e**, which has both the highest rate and the highest selectivity towards the desired product. The observed influence of the substituents of the ligand on the rate of the reaction seems to correlate with the bulkiness

Table 4.3. Nickel-catalyzed Kumada cross-coupling of 4-bromoanisole and phenylmagnesium chloride at room temperature.<sup>a</sup>

Entry	Complex	Time to completion (h)	Yield (10 <sup>-2</sup> mmol) <sup>b</sup>			
			6	7	8	9
1	<b>3a</b>	1.25	72	39	19	3
2	<b>3b</b>	1.25	68	39	25	4
3	<b>3c</b>	1.5	70	35	23	4
4	<b>3d</b>	4.5	71	33	23	4
5	<b>3e</b>	1.25	82	27	12	4
6	<b>3f</b>	1.5	76	38	13	5
7	<b>3g</b>	6.5	70	37	19	6
8	<b>3h</b>	8	69	35	20	5
9	<b>3i</b>	1.5	76	34	16	5
10	<b>3j</b>	1.25	76	38	12	5
11	<b>3k</b> <sup>c</sup>	50	33	33	10	1
12	<b>3l</b> <sup>d</sup>	90	59	41	15	1
13	<b>I</b> <sup>e</sup>	68	80	25	4	2

<sup>a</sup> Reaction conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylmagnesium chloride (25 w% in THF), 0.03 mmol catalyst, 1 mL THF, room temperature; <sup>b</sup> GC yields, average of two runs; <sup>c</sup> 43% conversion after 50 h; <sup>d</sup> 74% conversion after 90 h; <sup>e</sup> 88% conversion after 68 h.

of the side group. It appears that the side groups having more bulk close to the nickel center favor the rate of the reaction. A possible added effect of the benzyl side groups of complex **3e** may be that these may have a stacking interaction with the reagents. This effect is not observed with the phenyl substituents of complex **3f** because these point away from the nickel center and are not flexible enough to move closer to the reaction center. The order observed in the influence of the bridging moiety on the rate shows that the reaction rate benefits from longer and more rigid bridges.

The complexes **3a-j** are also active catalysts in the coupling of 4-bromoanisole; the effect of the better leaving group is reflected in the higher rates as compared to the reaction with the aryl chloride (Table 4.3). Again, the rate of the reaction and the composition of the final mixture differ depending on the ligand structure, whereas the influence of the halide anion in the starting complex is negligible. Seven of the complexes are able to complete the reaction within 90 minutes. Only the isopropyl-substituted complex **3d** and the butyl-bridged complexes **3g,h** require more time to bring the reaction to completion. The selectivity towards the desired product **6** ranges from 68 to 82%. A comparison of different ligands shows that the N-substituents of the carbene ligands do not have a large influence on the course of the reaction; all yield roughly the same selectivity around 70%, with the benzyl group as a positive exception with 82% (entry 5). The bridging group does not appear to have a large influence on the selectivity. The positive exception here is the Si-bridged complex **3i**, with a selectivity of 76% (entry 9).

It appears that in the case of 4-bromoanisole the rate decreases when bulkier side

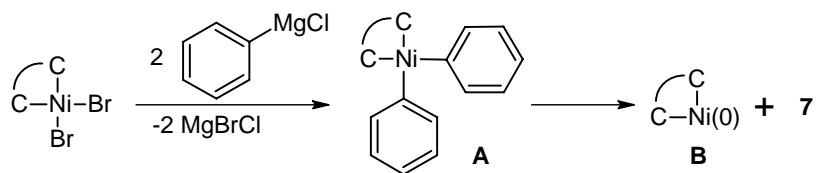
groups and longer bridges are used. For example, the lower rate of **3d** (Table 4.3, entry 4) may be attributed to the steric bulk of the isopropyl substituents on the ligand, which makes it more difficult for the reagents to approach the metal center. The high rate observed with complex **3e** may again be explained by stacking interaction of the benzyl substituents with the reagents. The slowest reaction is observed with complexes **3g** and **3h** (entries 7 and 8), which both contain the butyl-bridged ligand. Here, the lower rate may be a consequence of a difference in bite angle, even though the solid-state structure of **3g** has a bite angle that is only slightly larger compared to the other complexes. During the catalytic cycle, however, it is probable that the complex with the longer bridge adopts a conformation that could hinder the reaction. The bridge of **3j** is based on a four-carbon chain as well; however, the rigidity of the xylyl group may prevent the proposed unfavorable conformation.

A preliminary study showed that a reaction using the even more reactive 4-iodoanisole under the same conditions is completed in less than 10 minutes.

In addition to the bisNHC complexes described in catalysis above, nickel(II) complexes with macrocyclic bisNHC ligands (**3k**, **3l**) and the nickel cyclophane compound **I** reported by Baker *et al.*<sup>33</sup> were tested in the Kumada coupling of 4-bromoanisole, with the conditions used with the other bisNHC complexes. The results are included in Table 4.3. Unfortunately, these macrocyclic complexes are remarkably inactive in this reaction. For instance, complex **I** gave only 88% conversion of the starting aryl bromide to the desired product after 68 hours.

Numerous reports in literature describe the cross coupling of aryl halides and aryl Grignard reagents.<sup>49-54</sup> Unfortunately, making a comparison of the results is difficult, because of the various reaction conditions employed and the use of aryl halides and aryl Grignards with different substituents. In this study the reaction conditions used by Böhm *et al.* and Wolf *et al.* are followed, making it possible to compare our results to theirs.<sup>23-25</sup> Böhm *et al.*<sup>23</sup> obtained the highest rate and selectivity with  $\text{Ni}(\text{acac})_2$  *in situ* combined with the monodentate, bulky imidazolium salt  $\text{N,N}'\text{-bis}(2,6\text{-diisopropyl-phenyl})\text{imidazolium chloride}$  (IPr·HCl). Wolf *et al.*<sup>24, 25</sup> used zwitterionic nickel(II) complexes with a phosphane ligand linked to an imidazolium group ( $(\text{C}^{\text{P}}\text{NiBr}_3)$ ). The results of the most efficient catalysts of both reports are included in Table 4.2 (entries 11 and 12). Unfortunately, only the compositions of the reaction mixtures after 18 hours are reported, even though kinetic studies performed by Wolf *et al.* show that a conversion of 95% was reached within two hours. It appears therefore that our fastest catalysts (**3e** and **3j**, Table 4.2, entry 5 and 10) are more active than the Böhm system and less active than the fastest catalyst reported by Wolf. However, the most efficient catalyst in our work, **3e** (Table 4.2, entry 5) shows a higher selectivity for the desired cross-coupling product.

To test the stability of our catalyst type, a catalyst of average performance was chosen. Complex **3i** was used as catalyst for the coupling of 4-bromoanisole and phenylmagnesium chloride as in the other catalytic reactions. After GC analysis had shown full consumption of 4-bromoanisole, new substrates (1.0 mmol 4-bromoanisole and



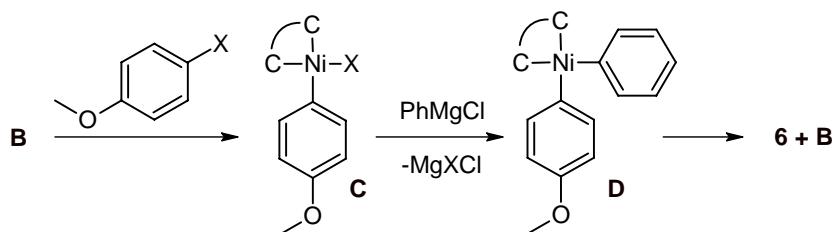
Scheme 4.4. Activation of catalyst precursor 3.

1.5 mmol Grignard reagent in 0.78 mL THF) were added. This was repeated 7 times over a period of 140 hours. The catalyst was found to be able to complete the reaction every time, indicating excellent stability. This resulted in a total turnover number of 230 mol [mol cat]<sup>-1</sup>, although the final batch took 10 hours to reach complete conversion. This lowering of the rate is most likely due to the accumulation of large amounts of product and magnesium salts, causing a substantial change in polarity and concentration of the reaction mixture.

#### 4.2.5 Mechanistic considerations

While monitoring the reaction of 4-chloroanisole with phenylmagnesium chloride by GC, it was observed that most of the biphenyl present at the end of the reaction had formed within the first ten minutes. This is in agreement with the mechanism leading to the active Ni(0) species as proposed by Kumada,<sup>55</sup> which results in biphenyl as a byproduct.<sup>56</sup> The proposed mechanism, adapted to the present catalytic system, is shown in Scheme 4.4. In the first step the two bromide ions of the precatalyst are replaced by phenyl groups of the Grignard reagent by transmetalation, yielding species A, which in the second step yields the active Ni(0) species B and biphenyl by reductive elimination. After activation the catalytic cycle (shown in Scheme 4.5) is followed as proposed in literature:<sup>55</sup> Oxidative addition of the 4-haloanisole yields species C, which undergoes a transmetalation step with the Grignard reagent to give bisaryl species D. Reductive elimination of 4-methoxybiphenyl 6 regenerates the nickel(0) species.

The results obtained for the catalysis with 4-chloroanisole (Table 4.2) show an increase in the rate of the reaction with more bulkiness of the ligand. This implies that the reductive elimination step from D to product 6 is rate determining, as the oxidative addition and the transmetalation would be hampered by a bulky ligand. For 4-bromoanisole the reaction is slowed down by a bulky ligand (Table 4.3), which implies that for this substrate either the oxidative addition or the transmetalation step is rate



Scheme 4.5. Transient species in the catalytic cycle of the Kumada coupling.

determining. Oxidative addition of aryl halides to analogous  $\text{Pd}(0)(\text{PR}_3)_2$  species has been calculated to be relatively easy,<sup>57</sup> and the strong  $\sigma$ -electron donating ability of the carbene ligands should make the oxidative addition more facile.<sup>11</sup> This leaves the transmetalation step to be rate limiting. Attempts to clarify this dependence of the rate-determining step on the halide and to elucidate the origin of the side products using density functional theory calculations are presented in Chapter 6. The relation between the shape and the bulk of the other ligands and the selectivity towards the various products with respect to the proposed mechanism remains uncertain.

### 4.3 Conclusion

In summary, several members of a novel class of  $\text{Ni}(\text{II})$  dihalide complexes with chelating bis(benzimidazol-2-ylidene) ligands have been synthesized and structurally characterized. In the complexes the biscarbene ligand is coordinated in a *cis*-configuration on a square-planar nickel center. The complexes are precursors for active catalysts for the Kumada coupling reaction of aryl bromides and chlorides with aryl Grignard reagents. The highest rate and selectivity are achieved using a benzyl-substituted, 1,3-propanediyl bridged biscarbene system. The trends observed in catalysis appear to indicate a change in the rate-determining step for the two different substrates.

### 4.4 Experimental Section

**General Procedures.** All syntheses were performed in air, unless noted otherwise. 1,4-Dioxane was dried by distillation from  $\text{CaH}_2$  and stored on molecular sieves under argon. N-phenylbenzimidazole,<sup>58</sup> N-n-propylbenzimidazole, N-isopropylbenzimidazole, N-benzylbenzimidazole,<sup>41</sup>  $\alpha,\alpha'$ -di(1-benzimidazolyl)-*o*-xylene,<sup>39</sup>  $\alpha,\alpha'$ -di(1-benzimidazolyl)-*m*-xylene,<sup>59</sup> bisbenzimidazolium salt **2k**<sup>33</sup> and bisbenzimidazolium salt **2l**,<sup>39</sup> were prepared according to literature procedures. Dehydrated  $\text{Ni}(\text{OAc})_2$  was obtained by heating  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  at 165 °C under a stream of argon. Other chemicals were obtained commercially and used as received.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX300. Chemical shifts are reported as referenced against the residual solvent signals and quoted in ppm relative to tetramethylsilane (TMS). IR spectra were recorded with a Perkin-Elmer FT-IR Paragon 1000 spectrophotometer equipped with a golden-gate ATR device, using the reflectance technique (4000-300  $\text{cm}^{-1}$ ; resolution 4  $\text{cm}^{-1}$ ). Elemental analyses were carried out with a Perkin-Elmer series II CHNS/O analyzer 2400. Halide contents were determined by potentiometric titration with silver nitrate according to the Volhard method. Electrospray mass spectra were recorded on a Finnigan TSQ-quantum instrument using an electrospray ionization technique (ESI-MS), using a water/acetonitrile or water/methanol mixture as solvent. 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*-butyl ether was used as an internal standard.

**General Procedure for the Synthesis of 1,1'-substituted bisbenzimidazolium salts (2).** In a Schlenk flask 1 equivalent of dihaloalkane and 2.1–2.2 equivalents of N-substituted

benzimidazole were dissolved in dry 1,4-dioxane under an argon atmosphere. The mixture was stirred at 100 °C for 16–24 h (for bromide salts) or 48 h (chloride salts), at which point the formation of a white precipitate was observed. The reaction mixture was cooled, filtered, washed thoroughly with THF and diethyl ether and dried *in vacuo*. The product was obtained as a white powder. The compound was further purified by recrystallization from MeOH/diethyl ether.

**1,1'-Dimethyl-3,3'-(1,3-propanediyl)bisbenzimidazolium dibromide (2a).** This ligand precursor was prepared as described in the general procedure, starting from 1,3-dibromopropane (1.22 mL, 12 mmol) and 1-methylbenzimidazole (3.44 g, 26 mmol) in 30 mL dry 1,4-dioxane. Yield: 4.45 g (80%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 9.88 (s, 2H, NCHN), 8.10 (m, 2H, Ar-H), 8.05 (m, 2H, Ar-H), 7.71 (m, 4H, Ar-H), 4.71 (t, 4H, *J* = 7 Hz, NCH<sub>2</sub>), 4.07 (s, 6H, CH<sub>3</sub>), 2.59 (t, 2H, *J* = 7 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 142.9 (NCHN), 131.8 (C<sub>q</sub>), 130.8 (C<sub>q</sub>), 126.5 (Ar), 126.4 (Ar), 113.6 (Ar), 113.6 (Ar), 43.8 (NCH<sub>2</sub>), 33.3 (NCH<sub>3</sub>), 28.1 (CH<sub>2</sub>). IR (neat): 3014 (w), 1569 (m), 1488 (m), 1456 (m), 1353 (m), 1266 (m), 1202 (m), 1128 (m), 1008 (w), 764 (s), 600 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>4</sub>·0.5H<sub>2</sub>O: C, 48.02; H, 4.88; N, 11.79. Found: C, 48.02; H, 4.87; N, 12.10. ESI-MS: *m/z* 385 ([M – Br]<sup>+</sup>), 305 ([M – 2Br – H]<sup>+</sup>), 153 ([M – 2Br]<sup>2+</sup>, 100%).

**1,1'-Dimethyl-3,3'-(1,3-propanediyl)bisbenzimidazolium dichloride (2b).** The compound was obtained following the general procedure, starting from N-methylbenzimidazole (2.91 g, 22 mmol) and 1,3 dichloropropane (0.95 mL, 10 mmol) in 30 mL dry 1,4-dioxane. Yield: 2.15 g (57%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 10.18 (s, 2H, NCHN), 8.13 (m, 2H, Ar-H), 8.02 (m, 2H, Ar-H), 7.68 (m, 4H, Ar-H), 4.73 (t, 4H, *J* = 7 Hz, NCH<sub>2</sub>), 4.08 (s, 6H, CH<sub>3</sub>), 2.60 (t, 2H, *J* = 7 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 143.1 (NCHN), 131.8 (C<sub>q</sub>), 130.8 (C<sub>q</sub>), 126.5 (Ar), 126.4 (Ar), 113.6 (Ar), 113.6 (Ar), 43.7 (NCH<sub>2</sub>), 33.2 (NCH<sub>3</sub>), 28.1 (CH<sub>2</sub>). IR (neat): 2939 (w), 1564 (m), 1462 (m), 1414 (m), 1354 (m), 1198 (m), 1010 (m), 756 (s), 432 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>·2H<sub>2</sub>O: C, 55.21; H, 6.34; N, 13.55. Found: C, 55.45; H, 6.47; N, 13.79. ESI-MS: *m/z* 341 ([M – Cl]<sup>+</sup>), 205 ([M – 2Cl – H]<sup>+</sup>), 153 ([M – 2Cl]<sup>2+</sup>, 100%).

**1,1'-Di-n-propyl-3,3'-(1,3-propanediyl)bisbenzimidazolium dibromide (2c).** The compound was obtained following the general procedure, starting from 1-isopropylbenzimidazole (4.49 g, 28 mmol) and 1,3-dibromopropane (2.42 g, 12 mmol) in 25 mL dry dioxane. The product is obtained as a white powder. Yield: 4.42 g (71%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 10.08 (s, 2H, NCHN), 8.13 (m, 4H, Ar-H), 7.70 (m, 4H, Ar-H), 4.74 (t, 4H, *J* = 7 Hz, NCH<sub>2</sub>), 4.50 (t, 4H, *J* = 7 Hz, NCH<sub>2</sub>), 2.65 (quint, 2H, *J* = 7 Hz, CH<sub>2</sub>), 1.89 (hex, 4H, *J* = 7 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 0.92 (t, 6H, *J* = 7 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 142.1 (NCHN), 131.1 (2 × C<sub>q</sub>), 126.5 (Ar), 126.4 (Ar), 113.6 (2 × Ar), 48.1 (NCH<sub>2</sub>), 43.9 (NCH<sub>2</sub>), 27.9 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 10.6 (CH<sub>3</sub>). IR (neat): 3016 (w), 1564 (s), 1457 (m), 1431 (m), 1352 (w), 1211 (m), 1018 (w), 877 (w), 760 (s), 611 (m), 426 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>4</sub>·0.5H<sub>2</sub>O: C, 51.99; H, 5.88; N, 10.54. Found: C: 51.62; H, 5.80; N, 10.57. ESI-MS: *m/z* 443 ([M – Br]<sup>+</sup>), 361 ([M – 2Br – H]<sup>+</sup>), 319 ([M – 2Br – Pr]<sup>+</sup>), 201 ([M – 2Br – PrBim]<sup>+</sup>), 181 ([M – 2Br]<sup>2+</sup>, 100%).

**1,1'-Diisopropyl-3,3'-(1,3-propanediyl)bisbenzimidazolium dibromide (2d).** The compound was prepared following the general procedure, starting from 1-propylbenzimidazole (3.52 g, 22 mmol) and 1,3-dibromopropane (2.02 g, 10 mmol) in 25 mL dry dioxane. The product is obtained as a white powder. Yield: 4.49 g (86%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 10.07 (s, 2H, NCHN), 8.16 (m, 4H, Ar-H), 7.68 (m, 4H, Ar-H), 5.06 (sept, 2H, *J* = 7 Hz, NCH(CH<sub>3</sub>)<sub>2</sub>), 4.72 (t, 4H, *J* = 7 Hz, NCH<sub>2</sub>), 2.70 (quint, 2H, *J* = 7 Hz, CH<sub>2</sub>), 1.62 (d, 12H, *J* = 7 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K): δ 140.9 (NCHN), 131.3 (C<sub>q</sub>), 130.5 (C<sub>q</sub>), 126.6 (Ar), 126.5 (Ar), 114.0 (Ar), 113.8 (Ar), 50.6 (NCH), 44.0 (NCH<sub>2</sub>), 28.1 (CH<sub>2</sub>), 21.6 (CH<sub>3</sub>). IR (neat): 3020 (w), 2980 (w), 1557 (m), 1436

(m), 1241 (m), 1213 (m), 1098 (m), 835 (w), 761 (s), 748 (s), 615 (s), 421 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{30}\text{Br}_2\text{N}_4 \cdot 0.5\text{H}_2\text{O}$ : C, 51.99; H, 5.88; N, 10.54. Found: C, 51.77; H, 5.52; N, 10.59. ESI-MS:  $m/z$  443 ( $[\text{M} - \text{Br}]^+$ ), 361 ( $[\text{M} - 2\text{Br} - \text{H}]^+$ ), 319 ( $[\text{M} - 2\text{Br} - \text{i-PrBim}]^+$ ), 201 ( $[\text{M} - 2\text{Br} - \text{i-PrBim}]^+$ ), 181 ( $[\text{M} - 2\text{Br}]^{2+}$ , 100%).

**1,1'-Dibenzyl-3,3'-(1,3-propanediyl)bisbenzimidazolium dibromide (2e).** The compound was obtained following the general procedure, starting from 3 mmol 1,3-dibromopropane (0.31 mL, 3 mmol) and 1-benzylbenzimidazole (1.29 g, 6.2 mmol) in 10 mL dry 1,4-dioxane. Yield: 1.20 g (65%).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  10.07 (s, 2H, NCHN), 8.15 (m, 2H, Ar-H), 7.96 (m, 2H, Ar-H), 7.68 (m, 4H, Ar-H), 7.54 (m, 4H, Ar-H), 7.41 (m, 6H, Ar-H), 5.79 (s, 4H,  $\text{PhCH}_2\text{N}$ ), 4.73 (t, 4H,  $J = 7$  Hz, NCH<sub>2</sub>), 2.66 (t, 2H,  $J = 7$  Hz, CH<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  142.3 (NCHN), 135.1 (C<sub>q</sub>), 132.6 (C<sub>q</sub>), 132.1 (C<sub>q</sub>), 130.2 (Ar), 130.0 (Ar), 129.6 (Ar), 128.0 (Ar), 127.9 (Ar), 115.2 (Ar), 115.1 (Ar), 51.2 (CH<sub>2</sub>), 45.4 (CH<sub>2</sub>), 28.0 (CH<sub>2</sub>). IR (neat): 3026 (w), 1559 (s), 1456 (m), 1344 (m), 1184 (m), 1020 (w), 753 (s), 702 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{31}\text{H}_{30}\text{Br}_2\text{N}_4$ : C, 60.21; H, 4.89; N, 9.06. Found: C, 59.97; H, 4.51; N, 9.06. ESI-MS:  $m/z$  538 ( $[\text{M} - \text{Br}]^+$ ), 456 ( $[\text{M} - 2\text{Br} - \text{H}]^+$ ), 367 ( $[\text{M} - \text{BnBimPr}]^+$ ), 250 ( $[\text{M} - 2\text{Br} - \text{BnBim}]^+$ ), 299 ( $[\text{M} - 2\text{Br}]^{2+}$ , 100%).

**1,1'-Diphenyl-3,3'-(propanediyl)dibenzimidazolium dibromide (2f).** The compound was prepared following the general procedure starting from 1-phenylbenzimidazole (2.33 g, 12 mmol) and 1,3-dibromopropane (1.01 g, 5 mmol) in 15 mL dry dioxane. Yield: 2.12 g (72%).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  10.34 (s, 2H, NCHN), 8.27 (d, 2H, 8Hz, Ar-H), 7.90-7.70 (m, 16H, Ar-H), 4.87 (t, 4H,  $J = 7$  Hz, NCH<sub>2</sub>), 2.83 (t, 2H,  $J = 7$  Hz, CH<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  141.0 (NCHN), 133.1 (C<sub>q</sub>), 131.3 (C<sub>q</sub>), 131.1 (C<sub>q</sub>), 130.5 (Ar), 130.4 (Ar), 127.6 (Ar), 127.0 (Ar), 125.1 (Ar), 114.1 (Ar), 113.6 (Ar), 44.3 (NCH<sub>2</sub>), 27.6 (CH<sub>2</sub>). IR (neat): 3005 (w), 1559 (m), 1421 (w), 1236 (m), 1118 (w), 872 (m), 764 (s), 745 (s), 696 (s), 592 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{29}\text{H}_{26}\text{Br}_2\text{N}_4 \cdot 2\text{CH}_3\text{OH}$ : C, 56.89; H, 5.24; N, 8.56. Found: C, 56.66; H, 4.93; N, 8.89. ESI-MS:  $m/z$  511 ( $[\text{M} - \text{Br}]^+$ ), 429 ( $[\text{M} - 2\text{Br} - \text{H}]^+$ ), 215 ( $[\text{M} - 2\text{Br}]^{2+}$ , 100%).

**1,1'-Dimethyl-3,3'-(1,4-butanediyl)bisbenzimidazolium dibromide (2g).** The compound was prepared following the general procedure, starting from 1,4-dibromobutane (1.20 mL, 10 mmol) and 1-benzylbenzimidazole (3.17 g, 24 mmol) in 20 mL dry 1,4-dioxane. Yield: 4.02 g (84%).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  9.84 (s, 2H, NCHN), 8.10 (m, 2H, Ar-H), 8.02 (m, 2H, Ar-H), 7.69 (m, 4H, Ar-H), 4.57 (s, 4H, NCH<sub>2</sub>), 4.07 (s, 6H, NCH<sub>3</sub>), 1.99 (s, 4H, CH<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  144.0 (NCHN), 133.0 (C<sub>q</sub>), 132.1 (C<sub>q</sub>), 127.7 (Ar), 114.9 (Ar), 114.8 (Ar), 47.2 (NCH<sub>2</sub>), 34.6 (NCH<sub>3</sub>), 26.8 (CH<sub>2</sub>). IR (neat): 2961 (m), 1620 (w), 1568 (m), 1460 (m), 1355 (m), 1221 (m), 759 (s), 567 (m), 426 (m)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{24}\text{Br}_2\text{N}_4 \cdot \text{H}_2\text{O}$ : C, 48.21; H, 5.26; N, 11.24. Found: C, 48.06; H, 5.36; N, 11.20. ESI-MS:  $m/z$  399 ( $[\text{M} - \text{Br}]^+$ ), 319 ( $[\text{M} - 2\text{Br} - \text{H}]^+$ ), 160 ( $[\text{M} - 2\text{Br}]^{2+}$ , 100%).

**1,1'-Dimethyl-3,3'-(1,4-butanediyl)bisbenzimidazolium dichloride (2h).** The compound was prepared following the general procedure, starting from 1,4-dichlorobutane (1.46 g, 11.5 mmol) and 1-benzylbenzimidazole (3.5 g, 26.5 mmol) in 20 mL dry 1,4-dioxane. Yield: 2.40 g (61%).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  10.12 (NCHN), 8.10 (m, 2H, Ar-H), 8.01 (m, 2H, Ar-H), 7.66 (m, 4H, Ar-H), 4.61 (t, 4H,  $J = 7$  Hz, NCH<sub>2</sub>), 4.08 (s, 6H, NCH<sub>3</sub>), 2.01 (t, 4H,  $J = 7$  Hz, CH<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ , 300 K):  $\delta$  143.0 (NCHN), 131.8 (C<sub>q</sub>), 130.9 (C<sub>q</sub>), 126.4 (2  $\times$  Ar), 113.6 (Ar), 113.5 (Ar), 45.8 (NCH<sub>2</sub>), 33.2 (NCH<sub>3</sub>), 25.3 (CH<sub>2</sub>). IR (neat): 3397 (m), 3030 (m), 1622 (w), 1568 (s), 1464 (m), 1354 (m), 1219 (m), 1144 (w), 764 (s), 652 (m), 601 (m), 557 (m), 424 (s)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_4 \cdot 2\text{H}_2\text{O}$ : C, 56.21; H, 6.60; N, 13.11. Found: C, 56.47; H, 6.44; N, 13.13. ESI-MS:  $m/z$  355 ( $[\text{M} - \text{Cl}]^+$ ), 319 ( $[\text{M} - 2\text{Cl} - \text{H}]^+$ ), 160 ( $[\text{M} - 2\text{Cl}]^{2+}$ , 100%).

**1,1'-Dimethyl-3,3'-( $\alpha,\alpha'$ -tetramethylsilane)bisbenzimidazolium dichloride (2i).** The compound was prepared following the general procedure, starting from bis(chloromethyl)dimethylsilane (1.45 mL, 10 mmol) and 1-methylbenzimidazole (2.91 g, 22 mmol) in 15 mL of dry 1,4-dioxane. Yield: 3.58 g (85%).  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ , 300 K):  $\delta$  10.03 (s, 2H, NCHN), 8.16 (m, 2H, Ar-H), 8.01 (m, 2H, Ar-H), 7.66 (m, 4H, Ar-H), 4.53 (s, 4H, NCH<sub>2</sub>Si), 4.10 (s, 6H, NCH<sub>3</sub>), 0.19 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ , 300 K):  $\delta$  142.1 (NCHN), 131.8 (2  $\times$  C<sub>q</sub>), 126.3 (Ar), 126.1 (Ar), 113.7 (Ar), 113.4 (Ar), 35.4 (NCH<sub>2</sub>Si), 33.2 (NCH<sub>3</sub>), -5.0 (Si(CH<sub>3</sub>)<sub>2</sub>). IR (neat): 3018 (m), 2957 (m), 1613 (w), 1560 (m), 1470 (m), 1357 (m), 1147 (m), 857 (s), 818 (m), 766 (s) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>Si·H<sub>2</sub>O: C, 54.66; H, 6.42; N, 12.75. Found: C, 54.58; H, 6.51; N, 12.68. ESI-MS: *m/z* 385 ([M - Cl]<sup>+</sup>), 221 ([M - 2Cl - MeBim]<sup>+</sup>, 100%), 175 ([M - 2Cl]<sup>2+</sup>), 147 ([Me<sub>2</sub>Bim]<sup>+</sup>).

**1,1'-Dimethyl-3,3'-( $\alpha,\alpha'$ -o-xylylene)bisbenzimidazolium dibromide (2j).** The compound was prepared following the general procedure, starting from N-methylbenzimidazole (12 mmol, 1.59 g) and  $\alpha,\alpha'$ -dibromo-o-xylene (5 mmol, 1.32 g) in 20 mL dry 1,4-dioxane. Yield: 2.62 g (81%).  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ , 300 K):  $\delta$  9.71 (s, 2H, NCHN), 8.04 (s, 2H, *J* = 8 Hz, Ar-H), 7.93 (d, 2H, *J* = 8 Hz, Ar-H), 7.67 (m, 4H, Ar-H), 7.42 (m, 4H, Ar-H), 7.24 (m, 4H, Ar-H), 6.05 (s, 4H, NCH<sub>2</sub>Ph), 4.06 (s, 6H, CH<sub>3</sub>).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ , 300 K):  $\delta$  144.3 (NCHN), 133.3 (C<sub>q</sub>), 133.2 (C<sub>q</sub>), 132.1 (C<sub>q</sub>), 130.7 (Ar), 130.2 (Ar), 128.0 (Ar), 127.9 (Ar), 115.0 (2 Ar), 48.7 (NCH<sub>2</sub>Ph), 34.7 (CH<sub>3</sub>). IR (neat): 3011 (m), 1568 (s), 1456 (m), 1381 (w), 1203 (m), 1093 (w), 1021 (w), 757 (s), 744 (s), 667 (w), 606 (w), 570 (m), 421 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>4</sub>·H<sub>2</sub>O: C, 52.77; H, 4.86; N, 10.26. Found: C, 52.74; H, 4.87; N, 10.35. ESI-MS: *m/z* 449 ([M - Br]<sup>+</sup>), 367 ([M - 2Br - H]<sup>+</sup>), 184 ([M - 2Br]<sup>2+</sup>, 100%).

**1,1'-(1,4-butanediyl)-3,3'-( $\alpha,\alpha'$ -m-xylylene)dibenzimidazolium bromide (2m).** To a solution of  $\alpha,\alpha'$ -di(1-benzimidazolyl)-*m*-xylene (0.60 g, 1.78 mmol) in 400 mL degassed acetonitrile was added 1,4-dibromobutane (5.2 g, 24 mmol) and the resulting mixture was refluxed for 4 days. The volume was then reduced *in vacuo* to 25 mL and cooled. The white precipitated that formed was collected by filtration and washed with acetonitrile and diethyl ether. Yield: 0.74 g (75%).  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ , 300 K):  $\delta$  9.70 (s, 2H, NCHN), 8.20 (m, 4H, Ar-H), 7.72 (m, 6H, Ar-H), 7.53 (t, 1H, *J* = 8 Hz, Ar-H), 7.08 (s, 1H, Ar-H), 5.75 (s, 4H, CH<sub>2</sub>Xy), 4.53 (broad s, 4H, NCH<sub>2</sub>), 1.77 (broad s, 4H, CH<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ , 300 K):  $\delta$  141.8 (NCHN), 135.7 (C<sub>q</sub>), 132.2 (C<sub>q</sub>), 131.0 (C<sub>q</sub>), 129.4 (Ar-C), 129.3 (Ar-C), 126.8 (Ar-C), 126.7 (Ar-C), 125.8 (Ar-C), 113.6 (Ar-C), 113.5 (Ar-C), 49.2 (NCH<sub>2</sub>), 45.1 (NCH<sub>2</sub>), 26.8 (CH<sub>2</sub>). IR (neat): 2959 (w), 1558 (s), 1448 (m), 1423 (m), 1376 (m), 1189 (s), 1015 (m), 821 (m), 798 (m), 752 (s), 427 (s) cm<sup>-1</sup>. ESI-MS: *m/z* 197 ([M - 2Br]<sup>2+</sup>, 100%), 218 ([M - 2Br + MeCN]<sup>2+</sup>), 393 ([M - 2Br - H]<sup>+</sup>), 475 ([M - Br]<sup>+</sup>). Anal. Calcd for C<sub>26</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>4</sub>·1.5H<sub>2</sub>O: C, 53.72; H, 5.03; N, 9.64. Found: C, 54.01; H, 5.30; N, 9.83.

**General procedure for the synthesis of nickel complexes (3).** Bisbenzimidazolium salt **2**, nickel(II) acetate and tetrabutylammonium halide were mixed and heated under vacuum in a 10 mL flask at 60 °C for 1 h, followed by heating under vacuum at 128 °C for 3 – 4 h. After cooling, the reaction mixture was triturated with water; the resulting solid was collected by filtration and washed with water. The complexes were further purified by dissolving the crude product in dichloromethane and washing the solution with water and saturated sodium halide solution. After the organic phase was dried with magnesium sulfate, the solution was concentrated *in vacuo* and the complex was precipitated with diethyl ether, filtered and dried *in vacuo*.

**Dibromido-(1,1'-dimethyl-3,3'-(1,3-propanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3a).** The complex was obtained as a yellow solid following the general procedure, starting from 0.47 g (1.0 mmol) bisbenzimidazolium salt **2a**, 1.0 mmol Ni(OAc)<sub>2</sub> (0.18 g) and 2.0 g

tetrabutylammonium bromide. Yield: 0.35 g (67%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  7.61 (m, 2H, Ar-H), 7.49 (m, 2H, Ar-H), 7.22 (m, 4H, Ar-H), 5.96 (broad s, 2H, NCH<sub>2</sub>), 5.00 (broad d, 2H, *J* = 11 Hz, NCH<sub>2</sub>), 4.60 (s, 6H, CH<sub>3</sub>), 2.72 (broad s, 1H, CH<sub>2</sub>), 1.93 (broad s, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  134.3 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 122.8 (Ar), 122.7 (Ar), 110.2 (Ar), 109.8 (Ar), 48.4 (NCH<sub>2</sub>), 35.0 (CH<sub>3</sub>), 28.0 (CH<sub>2</sub>). Ni-C could not be observed due to peak broadening. IR (neat): 3504 (w), 3037 (w), 2957 (w), 1457 (m), 1442 (m), 1394 (m), 1370 (m), 1340 (m), 1231 (w), 1134 (w), 1036 (w), 966 (w), 795 (w), 744 (s), 701 (m), 558 (m), 432 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>4</sub>Ni: C, 43.64; H, 3.85; N, 10.71. Found: C, 43.91; H, 3.95; N, 11.06. ESI-MS: *m/z* 483 ([M – Br + MeCN]<sup>+</sup>, 100%), 340 ([M – 2Br + OH]<sup>+</sup>). Crystals suitable for X-ray crystal structure determination were obtained by slow evaporation of a solution of the crude complex in dichloromethane/diethyl ether.

**Dichlorido-(1,1'-dimethyl-3,3'-(1,3-propanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3b).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2b** (0.28 g, 0.75 mmol), Ni(OAc)<sub>2</sub> (0.13 g, 0.75 mmol) and 2.0 g tetrabutylammonium chloride. Yield: 0.19 g (58%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  7.61 (m, 2H, Ar-H), 7.50 (m, 2H, Ar-H), 7.21 (m, 4H, Ar-H), 5.97 (broad s, 2H, NCH<sub>2</sub>), 4.97 (broad d, 2H, *J* = 11 Hz, NCH<sub>2</sub>), 4.60 (s, 6H, CH<sub>3</sub>), 2.72 (broad s, 1H, CH<sub>2</sub>), 1.90 (broad s, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  134.3 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 122.8 (Ar), 122.7 (Ar), 110.2 (Ar), 109.7 (Ar), 48.3 (NCH<sub>2</sub>), 35.0 (CH<sub>3</sub>), 28.0 (CH<sub>2</sub>). Ni-C could not be observed due to peak broadening. IR (neat): 2923 (m), 2854 (m), 1611 (w), 1462 (s), 1437 (s), 1393 (s), 1370 (s), 1338 (m), 1230 (w), 1127 (m), 1091 (m), 1034 (m), 967 (w), 859 (w), 795 (w), 736 (s), 560 (m), 435 (m) cm<sup>-1</sup>. Anal. Calcd. For C<sub>19</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>4</sub>Ni·H<sub>2</sub>O: C, 50.49; H, 4.91; N, 12.39. Found: C, 50.69; H, 5.18; N, 12.55. ESI-MS: *m/z* 438 ([M – Cl + MeCN]<sup>+</sup>, 100%), 340 ([M – 2Cl + OH]<sup>+</sup>).

**Dibromido-(1,1'-di-n-propyl-3,3'-(1,3-propanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3c).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2c** (0.52 g, 1.0 mmol), Ni(OAc)<sub>2</sub> (0.18 g, 1.0 mmol) and 2.0 g tetrabutylammonium bromide. Yield: 0.37 g (64%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  7.60 (m, 4H, Ar-H), 7.21 (m, 4H, Ar-H), 6.05 (bs, 2H, NCH<sub>2</sub>), 5.41 (m, 2H, NCH<sub>2</sub>), 4.98 (m, 2H, NCH<sub>2</sub>), 4.86 (m, 2H, NCH<sub>2</sub>), 2.71 (m, 1H, CH<sub>2</sub>), 2.06 (m, 3H, CH<sub>2</sub>), 1.84 (m, 2H, CH<sub>2</sub>), 1.15 (t, 6H, *J* = 7 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  134.5 (C<sub>q</sub>), 133.3 (C<sub>q</sub>), 122.9 (Ar), 122.7 (Ar), 110.9 (Ar), 110.1 (Ar), 50.3 (NCH<sub>2</sub>), 48.55 (NCH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 22.04 (CH<sub>2</sub>), 11.2 (CH<sub>3</sub>). IR (neat): 2960 (w), 1479 (m), 1455 (m), 1400 (s), 1214 (m), 1135 (m), 1044 (m), 1019 (m), 968 (w), 857 (w), 760 (s), 742 (s), 578 (w), 435 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>23</sub>H<sub>28</sub>Br<sub>2</sub>N<sub>4</sub>Ni·0.1CH<sub>2</sub>Cl<sub>2</sub>: C, 47.23; H, 4.84; N, 9.54. Found: C, 47.11; H, 4.79; N, 9.60. ESI-MS: *m/z* 540 ([M – Br + MeCN]<sup>+</sup>, 100%), 435 ([M – 2Br + OH]<sup>+</sup>).

**Dibromido-(1,1'-diisopropyl-3,3'-(1,3-propanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3d).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2d** (0.52 g, 1.0 mmol), Ni(OAc)<sub>2</sub> (0.18 g, 1.0 mmol) and 2.0 g tetrabutylammonium bromide. Yield: 0.34 g (59%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  7.60 (m, 4H, Ar-H), 7.24 (m, 4H, Ar-H), 6.68 (m, 1H, NCH or NCH<sub>2</sub>), 6.05 (m, 1H, NCH or NCH<sub>2</sub>), 5.75 (m, 1H, NCH or NCH<sub>2</sub>), 5.35 (m, 1H, NCH or NCH<sub>2</sub>), 5.01 (m, 2H, NCH or NCH<sub>2</sub>), 2.72 (m, 1H, CH<sub>2</sub>), 2.05 (m, 1H, CH<sub>2</sub>), 1.87 (m, 6H, CH<sub>3</sub>), 1.66 (m, 6H, CH<sub>3</sub>). Due to the poor solubility in regular solvents, no <sup>13</sup>C NMR spectrum was obtained. IR (neat): 3385 (w), 2978 (w), 1463 (m), 1403 (s), 1294 (m), 1137 (m), 1092 (m), 742 (s), 556 (m), 432 (m) cm<sup>-1</sup>. Anal. Calcd for

$C_{23}H_{28}Br_2N_4Ni \cdot 0.5CH_2Cl_2$ : C, 45.42; H, 4.70; N, 9.02. Found: C, 45.59; H, 4.45; N, 9.21. ESI-MS:  $m/z$  496 ( $[M - Br]^+$ , 100%).

**Dibromido-(1,1'-dibenzyl-3,3'-(1,3-propanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3e).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2e** (0.46 g, 0.75 mmol),  $Ni(OAc)_2$  (0.13 g, 0.75 mmol) and 2.0 g tetrabutylammonium bromide. Yield: 0.31 g (41%).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  7.67 (d, 2H,  $J = 8$  Hz, Ar-H), 7.30–6.75 (m, 18H, Ar-H +  $PhCH_2N$ ), 6.20 (bs, 2H,  $PhCH_2N$ ), 5.57 (bs, 2H,  $NCH_2$ ), 5.08 (bs, 2H,  $NCH_2$ ), 2.79 (bs, 1H,  $CH_2CH_2CH_2$ ), 2.15 (bs, 1H,  $CH_2CH_2CH_2$ ).  $^{13}C$  NMR (75 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  135.5 ( $C_q$ ), 134.8 ( $C_q$ ), 133.1 ( $C_q$ ), 128.5 (Ar), 127.8 (Ar), 127.4 (Ar), 122.9 (Ar), 122.7 (Ar), 111.1 (Ar), 110.3 (Ar), 51.9 ( $CH_2$ ), 48.7 ( $CH_2$ ), 28.6 ( $CH_2$ ). Ni-C could not be observed due to peak broadening. IR (neat): 2960 (m), 2872 (m), 1607 (w), 1458 (m), 1404 (s), 1361 (m), 1203 (m), 1034 (m), 739 (s), 699 (m), 434 (m)  $cm^{-1}$ . Anal. Calcd for  $C_{31}H_{28}Br_2N_4Ni \cdot 0.1CH_2Cl_2$ : C, 54.64; H, 4.16; N, 8.20. Found: C, 54.65; H, 3.90; N, 8.39. ESI-MS:  $m/z$  532 ( $[M - 2Br + OH]^+$ ), 592 ( $[M - Br]^+$ , 100%). Crystals suitable for X-ray crystal structure determination were obtained by slow evaporation of a solution of the crude complex in dichloromethane/diethyl ether.

**Dibromido-(1,1'-diphenyl-3,3'-(1,3-propanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3f).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2f** (0.59 g, 1.0 mmol),  $Ni(OAc)_2$  (0.18 g, 1.0 mmol) and 2.5 g tetrabutylammonium bromide. Yield: 0.38 g (59%).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  7.99 – 7.77 (m, 6H, Ar-H), 7.55 – 7.13 (m, 12H, Ar-H), 6.63 (bs, 2H,  $NCH_2$ ), 5.20 (m, 2H,  $NCH_2$ ), 2.96 (bs, 1H,  $CH_2$ ), 2.28 (bs, 1H,  $CH_2$ ).  $^{13}C$  NMR (75 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  137.2 ( $C_q$ ), 135.6 ( $2 \times C_q$ ), 130.7 (Ar), 129.7 (Ar), 127.1 (Ar), 124.9 (Ar), 124.5 (Ar), 112.0 (Ar), 111.5 (Ar), 50.2 ( $NCH_2$ ), 26.4 ( $CH_2$ ). IR (neat): 2961 (m), 1597 (w), 1502 (m), 1474 (m), 1402 (m), 1369 (m), 1221 (w), 1091 (w), 1026 (w), 810 (w), 750 (s), 696 (s), 4901 (w), 438 (w)  $cm^{-1}$ . Anal. Calcd for  $C_{29}H_{24}Br_2N_4Ni \cdot 0.2Et_2O$ : C, 54.08; H, 3.96; N, 8.46. Found: C, 53.96; H, 4.15; N, 8.45. ESI-MS:  $m/z$  607 ( $[M - Br + ACN]^+$ , 100%).

**Dibromido-(1,1'-dimethyl-3,3'-(1,4-butanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3g).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2g** (0.24 g, 0.5 mmol),  $Ni(OAc)_2$  (0.09 g, 0.5 mmol) and 3.0 g tetrabutylammonium bromide. Yield: 0.12 g (45%).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  7.63 (m, 2H, Ar-H), 7.55 (m, 2H, Ar-H), 7.25 (m, 4H, Ar-H), 6.30 (m, 2H,  $NCH_2$ ), 4.71 (m, 2H,  $NCH_2$ ), 4.61 (s, 6H,  $NCH_3$ ), 2.36 (m, 2H,  $CH_2$ ), 1.31 (m, 2H,  $CH_2$ ).  $^{13}C$  NMR (75 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  135.2 ( $C_q$ ), 133.6 ( $C_q$ ), 122.9 (Ar), 122.8 (Ar), 110.4 (Ar), 110.2 (Ar), 43.3 ( $NCH_2$ ), 35.3 ( $NCH_3$ ), 24.1 ( $CH_2$ ). Ni-C could not be observed due to peak broadening. IR (neat): 2940 (w), 1612 (w), 1464 (m), 1439 (m), 1393 (m), 1342 (m), 1189 (m), 745 (s), 440 (m)  $cm^{-1}$ . Anal. Calcd for  $C_{20}H_{22}Br_2N_4Ni \cdot 0.75CH_2Cl_2$ : C, 41.49; H, 3.94; N, 9.33. Found: C, 41.41; H, 3.66; N, 9.34. ESI-MS:  $m/z$  394 ( $[M - 2Br + OH]^+$ ), 498 ( $[M - Br + MeCN]^+$ , 100%). Crystals suitable for X-ray crystal structure determination were obtained by slow evaporation of a solution of the crude complex in dichloromethane/acetonitrile.

**Dichlorido-(1,1'-dimethyl-3,3'-(1,4-butanediyl)dibenzimidazol-2,2'-diylidene)nickel(II) (3h).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2h** (0.39 g, 1.0 mmol),  $Ni(OAc)_2$  (0.18 g, 1.0 mmol) and 3.0 g tetrabutylammonium chloride. This complex is soluble in water and therefore the purification step after the trituration with water was omitted. Yield: 0.34 g (77%).  $^1H$  NMR (300 MHz,  $DMSO-d_6$ , 300 K):  $\delta$  7.61 (m, 2H, Ar-H), 7.55 (m, 2H, Ar-H), 7.23 (m, 4H, Ar-H), 6.34 (m, 2H,  $NCH_2$ ), 4.75 (m, 2H,  $NCH_2$ ), 4.62 (s, 6H,  $NCH_3$ ), 2.36 (m, 2H,  $CH_2$ ), 1.29 (m, 2H,  $CH_2$ ).  $^{13}C$  NMR (75

MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  134.9 (C<sub>q</sub>), 133.4 (C<sub>q</sub>), 122.8 (Ar), 122.7 (Ar), 110.2 (Ar), 110.1 (Ar), 43.2 (NCH<sub>2</sub>), 35.1 (NCH<sub>3</sub>), 24.1 (CH<sub>2</sub>). Ni-C could not be observed due to peak broadening. IR (neat): 3403 (w), 2961 (w), 1471 (m), 1444 (m), 1395 (s), 1343 (m), 1192 (m), 1127 (w), 1008 (w), 808 (w), 752 (s), 745 (s), 580 (w), 445 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>4</sub>Ni·H<sub>2</sub>O·0.2Bu<sub>4</sub>NCl: C, 53.42; H, 6.03; N, 11.28. Found: C, 53.56; H, 6.18; N, 11.59. ESI-MS: *m/z* 452 ([M - Cl + MeCN]<sup>+</sup>, 100%).

**Dibromido-(1,1'-dimethyl-3,3'-( $\alpha,\alpha'$ -tetramethylsilane)dibenzimidazol-2,2'-diylidene)nickel(II) (3i).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2i** (0.32 g, 0.75 mmol), Ni(OAc)<sub>2</sub> (0.13 g, 0.75 mmol), potassium bromide (0.5 g) and 2.0 g tetrabutylammonium bromide. Yield: 0.29 g (68%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  7.71 (m, 2H, Ar-H), 7.50 (m, 2H, Ar-H), 7.22 (m, 4H, Ar-H), 5.47 (d, 2H, *J* = 16 Hz, NCH<sub>2</sub>Si), 4.67 (s, 6H, NCH<sub>3</sub>), 4.35 (d, 2H, *J* = 16 Hz, NCH<sub>2</sub>Si), 0.66 (s, 3H, SiCH<sub>3</sub>), -0.49 (s, 3H, SiCH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  135.0 (C<sub>q</sub>), 134.4 (C<sub>q</sub>), 122.6 (Ar), 122.4 (Ar), 110.2 (2 Ar), 38.2 (NCH<sub>2</sub>Si), 35.5 (NCH<sub>3</sub>), -5.4 (SiCH<sub>3</sub>), -7.6 (SiCH<sub>3</sub>). Ni-C could not be observed due to peak broadening. IR (neat): 3048 (w), 2955 (w), 1609 (w), 1438 (m), 1385 (m), 1249 (w), 863 (m), 741 (s), 695 (w), 439 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>4</sub>NiSi·0.7Et<sub>2</sub>O: C, 44.25; H, 5.05; N, 9.05. Found: C, 44.55; H, 4.99; N, 9.87. ESI-MS: *m/z* 423 ([M - 2Br + OH]<sup>+</sup>), 484 ([M - Br]<sup>+</sup>, 100%). Crystals suitable for X-ray crystal structure determination were obtained by slow evaporation of a solution of the crude complex in dichloromethane/acetonitrile.

**Dibromido-(1,1'-dimethyl-3,3'-( $\alpha,\alpha'$ -o-xylylene)dibenzimidazol-2,2'-diylidene)nickel(II) (3j).** The complex was obtained as a yellow solid following the general procedure, starting from bisbenzimidazolium salt **2j** (0.53 g, 1.0 mmol), Ni(OAc)<sub>2</sub> (0.18 g, 1.0 mmol) and 2.0 g tetrabutylammonium bromide. Yield: 0.42 g (72%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  8.20 (m, 2H, Ar-H), 8.07 (d, 2H, *J* = 8 Hz, Ar-H), 7.88 (d, 2H, *J* = 15 Hz, NCH<sub>2</sub>), 7.50 (m, 4H, Ar-H), 7.28 (m, 4H, Ar-H), 5.78 (d, 2H, *J* = 15 Hz, NCH<sub>2</sub>), 4.67 (s, 6H, NCH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  135.3 (C<sub>q</sub>), 135.1 (C<sub>q</sub>), 133.9 (C<sub>q</sub>), 133.6 (Ar), 129.2 (Ar), 123.0 (Ar), 122.9 (Ar), 111.3 (Ar), 110.5 (Ar), 50.0 (CH<sub>2</sub>), 35.7 (CH<sub>3</sub>). Ni-C could not be observed due to peak broadening. IR (neat): 3062 (w), 1616 (w), 1463 (m), 1436 (m), 1395 (m), 1340 (m), 1214 (w), 1194 (w), 1095 (w), 1016 (w), 788 (m), 740 (s), 700 (w), 668 (w), 580 (w), 549 (w), 436 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>4</sub>Ni·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 46.90; H, 3.69; N, 8.93. Found: C, 47.08; H, 3.70; N, 8.99. ESI-MS: *m/z* 442 ([M - 2Br + OH]<sup>+</sup>), 502 ([M - Br]<sup>+</sup>, 100%).

**Dichlorido-(1,1'-3,3'-bis( $\alpha,\alpha'$ -o-xylylene)dibenzimidazol-2,2'-diylidene)nickel(II) (3k).** Following an adaptation of the procedure reported for the synthesis of **I** by Baker *et al.*<sup>33</sup> a solution of benzimidazolium bromide **2k** (1.0 g, 1.7 mmol) in 25 mL methanol was added to a solution of KPF<sub>6</sub> (1.5 g, 8.1 mmol) in 25 mL of the same solvent and stirred at room temperature for several hours. The white precipitate that formed was isolated by filtration and dried *in vacuo*. A solution of this PF<sub>6</sub> salt (0.36 g, 0.50 mmol), NaOAc (0.09 g, 1.10 mmol) and NiCl<sub>2</sub> (65 mg, 0.50 mmol) in 12 mL of degassed DMF was stirred for 72 h at 90 °C. The resulting mixture was evaporated to dryness, dissolved in 200 mL dichloromethane and washed twice with water and once with brine. After drying with magnesium sulfate, most of the solvent was removed *in vacuo* and the product was precipitated by addition of diethyl ether, filtered and dried *in vacuo*. The compound was obtained as a yellow solid and was further purified by recrystallization from dichloromethane/diethyl ether. Yield: 0.16 g (55%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 300 K):  $\delta$  7.88 (d, 4H, *J* = 15 Hz, CH<sub>2</sub>), 7.68 (m, 4H, Ar-H), 7.41 (m, 4H, Ar-H), 7.19 (m, 4H, Ar-H), 6.91 (m, 4H, Ar-H), 5.28 (d, 4H, *J* = 15 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>, 300 K):  $\delta$  134.8 (2 × C<sub>q</sub>), 133.9 (C<sub>Ar</sub>), 129.8 (C<sub>Ar</sub>), 123.2 (C<sub>Ar</sub>), 110.8 (C<sub>Ar</sub>), 51.9 (CH<sub>2</sub>). IR (neat): 3063 (w), 1475 (w), 1458 (w), 1413 (m),

1336 (w), 1020 (w), 834 (s), 736 (s), 556 (s)  $\text{cm}^{-1}$ . Anal. Calcd. For  $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_4\text{Ni}\cdot 2.5\text{H}_2\text{O}$ : C, 58.57; H, 4.75; N, 9.11. Found: C, 58.65; H, 4.51; N, 9.32. ESI-MS:  $m/z$  533 ( $[\text{M} - \text{Cl}]^+$ , 100%).

**Dibromido-(1,1'-(1,4-butanediyl)-3,3'-( $\alpha,\alpha'$ -o-xylylene)dibenzimidazol-2,2'-diylidene)nickel(II) (3l).** This compound was prepared according to the general procedure, starting from macrocyclic bisbenzimidazolium bromide **2l** (0.30 g, 0.54 mmol),  $\text{Ni}(\text{OAc})_2$  (96 mg, 0.54 mmol) and 1.0 g of tetrabutylammonium bromide and obtained as a yellow solid. Yield: 0.14 g (42%).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ , 300 K):  $\delta$  8.21 (m, 2H, Xy-H), 8.03 (d, 2H,  $J = 7$  Hz, Bim-H), 7.89 (d, 2H,  $J = 15$  Hz, XyCH<sub>2</sub>), 7.61 (d, 2H,  $J = 7$  Hz, Bim-H), 7.50 (m, 2H, Xy-H), 7.26 (m, 4H, Bim-H), 6.37 (m, 2H, NCH<sub>2</sub>), 5.79 (d, 2H,  $J = 15$  Hz, XyCH<sub>2</sub>), 4.72 (d, 2H, NCH<sub>2</sub>), 2.40 (m, 2H, CH<sub>2</sub>), 1.24 (m, 2H, CH<sub>2</sub>).  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}-d_6$ , 300 K):  $\delta$  135.1 (C<sub>q</sub>), 134.1 (Ar-C), 134.0 (2  $\times$  C<sub>q</sub>), 129.3 (Ar-C), 123.2 (Ar-C), 123.0 (Ar-C), 111.6 (Ar-C), 110.6 (Ar-C), 50.2 (NCH<sub>2</sub>), 43.5 (NCH<sub>2</sub>), 24.5 (CH<sub>2</sub>). IR (neat): 2942 (s), 1478 (m), 1409 (s), 1338 (m), 1178 (m), 1008 (w), 786 (m), 742 (s), 668 (m), 428 (m)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{26}\text{H}_{24}\text{Br}_2\text{N}_4\text{Ni}\cdot 0.4\text{CH}_2\text{Cl}_2$ : C, 49.16; H, 3.88; N, 8.69. Found: C, 49.07; H, 3.99; N, 8.47. ESI-MS:  $m/z$  571 ( $[\text{M} - \text{Br} + \text{MeCN}]^+$ , 100%).

**General procedure for the Kumada reaction.** At room temperature, 1.0 mmol of the appropriate 4-haloanisole was added to a solution or suspension of 0.03 mmol nickel complex in 1 mL dry THF under an argon atmosphere. A 25 wt% solution of phenylmagnesium chloride in THF (0.78 mL, 1.5 mmol) was added drop wise with stirring, changing the reaction mixture into a clear, brown solution. At regular intervals aliquots were taken, dissolved in aqueous ethanol and analyzed by gas chromatography. Samples were taken until full conversion was reached. All catalytic reactions were performed in duplicate and were found to be consistent.

To obtain the desired coupling product, water was added and the reaction mixture was extracted into ethyl acetate (3  $\times$  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.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were in agreement with the proposed structure,<sup>26</sup> and the GC retention time corresponded to that of a commercial sample.

**X-ray crystal structure determinations.** X-ray reflections were measured with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Nonius KappaCCD diffractometer with rotating anode at a temperature of 150 K. Integration of the reflections was performed with EvalCCD.<sup>60</sup> The structures were solved with automated Patterson methods (program DIRDIF-99<sup>61</sup> for **3a** and **3g**) or Direct Methods (program SIR-97 for **3e**,<sup>62</sup> SHELXS-97 for **3i**).<sup>63</sup> Refinement was performed with SHELXL-97 against  $F^2$  of all reflections.<sup>63</sup> Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry were performed with the PLATON program.<sup>64</sup>

The crystal of **3a** was non-merohedrally twinned with a twofold rotation about  $hkl$  (001) as twin operation. This twin law was taken into account during intensity integration and the HKLF5 structure refinement.<sup>65</sup> The twin fraction refined to 0.5053(11).

The crystal of **3e** contained large voids (648.6 Å<sup>3</sup> / unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the routine SQUEEZE of the program PLATON resulting in 228.8 electrons / unit cell.<sup>64</sup>

In the crystal structure of **3i** the methyl group at C33 was rotationally disordered.

Further details concerning the crystal structure determinations are given in Table 4.4.

Table 4.4. Selected crystallographic data for complexes **3a**, **3e**, **3g**, and **3i**.

	<b>3a</b>	<b>3e</b>	<b>3g</b>	<b>3i</b>
formula	C <sub>19</sub> H <sub>20</sub> Br <sub>2</sub> N <sub>4</sub> Ni · CH <sub>2</sub> Cl <sub>2</sub>	C <sub>31</sub> H <sub>28</sub> Br <sub>2</sub> N <sub>4</sub> Ni · CH <sub>2</sub> Cl <sub>2</sub> + disordered solvent	C <sub>20</sub> H <sub>22</sub> Br <sub>2</sub> N <sub>4</sub> Ni	C <sub>20</sub> H <sub>24</sub> Br <sub>2</sub> N <sub>4</sub> NiSi
Fw	607.85	760.03 <sup>a</sup>	536.95	567.05
crystal color	yellow	yellow	yellow	dark yellow
crystal size [mm <sup>3</sup> ]	0.42x0.15x0.13	0.45x0.27x0.15	0.66x0.12x0.06	0.42x0.31x0.27
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)	P2 <sub>1</sub> /c (no. 14)
a [Å]	10.885(2)	9.7277(4)	10.00749(19)	8.5452(2)
b [Å]	19.126(4)	15.0886(6)	14.1631(2)	17.5481(3)
c [Å]	15.216(3)	25.4183(9)	15.0239(2)	14.7896(3)
β [°]	133.513(4)	106.788(2)	106.392(1)	97.951(2)
V [Å <sup>3</sup> ]	2297.3(8)	3571.8(2)	2042.89(6)	2196.42(8)
Z	4	4	4	4
D <sub>x</sub> [g/cm <sup>3</sup> ]	1.757	1.413 <sup>a</sup>	1.746	1.715
(sin θ/λ) <sub>max</sub> [Å <sup>-1</sup> ]	0.61	0.61	0.65	0.65
refl.	41727 / 7247	54246 / 6591	34303 / 4693	45494
meas./unique				
μ [mm <sup>-1</sup> ]	4.570	2.955 <sup>a</sup>	4.874	4.590
abs. corr.	analytical	multi-scan	analytical	multi-scan
abs. corr. range	0.28-0.76	0.29-0.64	0.12-0.82	0.13-0.29
param./restraints	265 / 0	370 / 0	246 / 0	257 / 0
R1/wR2 [I>2σ(I)]	0.0637 / 0.1553	0.0579 / 0.1472	0.0514 / 0.1023	0.0275 / 0.0655
R1/wR2 [all refl.]	0.0849 / 0.1681	0.0673 / 0.1508	0.0686 / 0.1085	0.0372 / 0.0691
S	1.153	1.083	1.140	1.084
res. density [e/Å <sup>3</sup> ]	-1.59 / 2.20	-0.77 / 1.59	-1.25 / 1.46	-1.00 / 0.43

<sup>a</sup> Derived parameters do not contain the contribution of the disordered solvent.

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