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Formation of Homoleptic Tetracarbene versus *cis*-Chelating Dicarbene Complexes of Nickel(II) and Applications in Kumada–Corriu Couplings

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The formation of mono- versus bis(chelate) Ni^{II} complexes bearing N-heterocyclic dicarbene ligands can be controlled by the flexibility of the ligand bridge. A short methylene spacer exclusively gives rise to a dicationic bis(chelate) complex $[Ni(^{Me}CC^{meth})_2]Br_2$ (**1**), whereas a more flexible propylene spacer affords a neutral monochelate complex $[NiBr_2(^{Me}CC^{prop})]$ (**2**). Complex **2** was found to autoionize very slowly to the corresponding dicationic bis(chelate) over ca. 45 d in $[D_6]$dmso. The formation of the bis- versus monochelate complex can be attributed to the different stabilities of the resulting metallacycles. The catalytic activity of monochelate **2** was tested in the Kumada–Corriu coupling of aryl halides with arylmagnesium reagents at ambient temperature.

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Introduction

N-heterocyclic carbenes (NHCs) have become state-of the art ligands in organometallic chemistry, and many of their transition-metal complexes have found successful applications in homogeneous catalysis.[1] In this respect, Pd–NHC complexes are undoubtedly the most intensely studied type of complexes, and many different methods for their preparation have been established. In the simplest case, the reaction of 2 equiv. of azolium halides with $Pd(OAc)_2$ gives rise to a stable dihalido-dicarbene Pd^{II} complex of the type $[PdX_2(NHC)_2]$ (X = halide), in which the monodentate NHCs adopt either a *cis*- or *trans* configuration in a square-planar coordination geometry. The extension of this methodology to bridged diazolium salts usually results in neutral *cis*-$[PdX_2(diNHC)]$ complexes, which are versatile catalyst precursors as well. The *cis* arrangement of NHC ligands in such complexes should translate into a faster initiation of the catalyst due to their strong *trans* effect.[2] Notably, the analogous reaction of azolium salts with $Ni(OAc)_2$ only yields *trans*-$[NiX_2(NHC)_2]$ complexes,[3–6] and surprisingly, *cis* isomers remain unknown to date. Early attempts by Herrmann et al. to prepare *cis*-chelating dihalido-dicarbene complexes of Ni^{II} by employing methylene-bridged diimidazolium- or ditriazolium diiodides with various N-substituents were unsuccessful, and instead afforded homoleptic tetracarbene Ni^{II} complexes of the type $[Ni(diNHC)_2]I_2$.[7] The formation of the targeted neutral *cis*-$[NiI_2(diNHC)]$ complexes, which may lead to low-cost catalysts, was never observed. Although not specifically addressed by the authors, the formation of the dicationic bis(chelating) $[Ni(diNHC)_2]I_2$ complexes may be due to autoionization processes, which have been commonly observed for Ni diphosphane analogues.[8,9] However, by employing a more rigid dicarbene derived from an imidazolium-linked *ortho*-cyclophane, Baker and co-workers finally succeeded in the preparation of the only known *cis*-$[NiCl_2(diNHC)]$ complex, in which the two *cis*-carbene moieties are formally connected by two C_4 bridges.[10] Much of our research has focused on benzimidazole-derived NHCs, and we have recently established a methodology for the preparation of neutral dihalido-bis(benzimidazolin-2-ylidene) complexes of Ni^{II}.[5,6] In extension of this work, we herein report on the factors that determine the formation of dicationic bis(chelate) versus neutral, dibromido, monochelate complexes of Ni^{II}, and the catalytic activities of the latter in the Kumada–Corriu coupling reaction.

Results and Discussion

As reported recently, red complexes of the type *trans*-$[NiBr_2(NHC_{bim})_2]$ (NHC_{bim} = benzimidazolin-2-ylidene) can be conveniently prepared by reacting 2 equiv. benzimidazolium bromides with anhydrous $Ni(OAc)_2$ in molten tetrabutylammonium bromide (tbab).[5,6] A similar reaction with the methylene-bridged dibenzimidazolium salt $[^{Me}CC^{meth}H_2]Br_2$ (**A**),[11] on the other hand, yielded the white tetracarbene complex $[Ni(^{Me}CC^{meth})_2]Br_2$ (**1**), which dissolves in polar organic solvents such as dmso, MeOH and EtOH (sparingly), but proves to be insoluble in water and other common organic solvents (Scheme 1).

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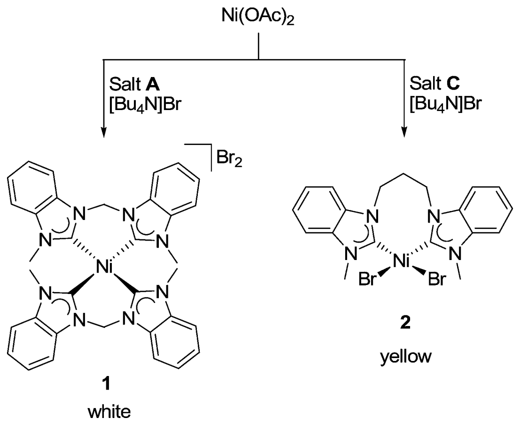


Scheme 1. Synthesis of bis(chelate) and monochelate complexes of Ni^{II}.

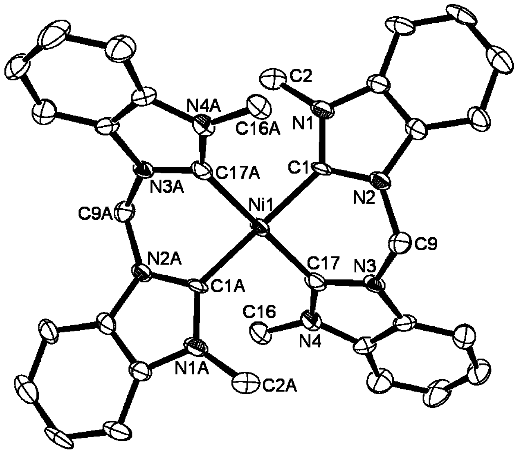


Figure 1. Molecular structure of the dicationic bis(chelate) complex of **1**·0.5H$_2$O showing 50% probability ellipsoids; hydrogen atoms, two bromide counteranions and half a water molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C1 1.891(6), Ni1–C17 1.906(6), N1–C1 1.361(7), N2–C1 1.365(7), N2–C9 1.456(7), N3–C9 1.443(7), N3–C17 1.362(8), N4–C17 1.364(8); C1–Ni1–C17 86.6(2), C1A–Ni1–C17 93.4(2), C1–Ni1–C17A 93.4(2), C1A–Ni1–C17A 86.6(2), N1–C1–N2 105.1(5), N3–C17–N4 105.3(5).

The positive mode ESI mass spectrum of **1** shows a base peak at *m*/*z* = 305 with an isotopic peak difference of 0.5 mass units, which is indicative of the bis(chelate) ion [Ni(^{Me}CC^{meth})$_2$]$^{2+}$. A less-intense isotopic envelope for the fragment [Ni(^{Me}CC^{meth})$_2$ + Br]$^+$ is also observed at *m*/*z* = 691. Its ^{1}H NMR spectrum in [D$_6$]dmso is rather simple and shows 2 doublets and 2 pseudotriplets for the aromatic protons of the carbene ligands. As reported for imidazole- and triazole-derived analogues, the protons for the methylene bridge are diastereotopic and their signals are shifted to lower field (δ = 7.65 and 7.59 ppm) upon coordination to the metal center. The carbene signal is found at δ = 183 ppm, which is, as expected, more downfield relative to those found for the corresponding imidazoline- and triazoline-derived analogues (170–174 ppm).[7,12] X-ray diffraction on single crystals obtained by slow evaporation of a concentrated MeOH solution finally confirmed the identity of **1**[13] as a dicationic bis(chelate) complex, and its molecular structure is depicted in Figure 1.

The asymmetric unit contains half of the dication, one bromide, and a quarter water molecule. The essentially square-planar dication of **1** adopts a *trans* double-boat conformation with Ni–C$_{carbene}$ distances of 1.891(6) (Ni1–C1) and 1.906(6) Å (Ni1–C17), which are in the same range as those found in the direct imidazolin-2-ylidene analogue.[7] The commonly observed perpendicular orientation of the carbene ring planes with respect to the ML$_4$ coordination plane is markedly less due to the rigid methylene bridge, and dihedral angles of 43.33° and 43.47°, respectively, are observed. The Pt^{II} complex with a macrocyclic tetracarbene ligand of crown-ether topology reported by Hahn et al.[14] is perhaps, in this respect, the closest complex, which bears C$_1$-bridged benzimidazolin-2-ylidene ligands. In this complex, the four C$_1$-bridges force the carbene planes to be almost coplanar to the MC$_4$ coordination plane (maximum angle 15.6°).

To determine whether the bridge length has any influence on the formation of bis(chelate) versus monochelate complexes, we attempted the reaction of dibenzimidazolium salts [^{Me}CC^{eth}H$_2$]Br$_2$ (**B**)[11] and [^{Me}CC^{prop}H$_2$]Br$_2$ (**C**) bearing simple C$_2$ and C$_3$ alkyl bridges, respectively, with Ni(OAc)$_2$ under the same conditions. However, salt **B** did not readily react, and only traces of the corresponding monochelate [NiBr$_2$(^{Me}CC^{eth})] could be identified by ESI mass spectrometry at *m*/*z* = 507. Extension of the reaction time to 18 h also proved unsuccessful, and, in all cases, mainly the unreacted salt precursor was reisolated. The difficulty in directly converting ethylene-bridged diazolium halides to the corresponding chelating metal–dicarbene complexes has also been observed for palladium.[15,16] Attempts to synthesize the desired complex by Ag–NHC transfer reactions were unsuccessful and led to insoluble mixtures, which hampered proper characterization. It is likely that these insoluble mixtures contain coordination polymers.

Interestingly, reaction with salt precursor **C** afforded the neutral monochelate complex [NiBr$_2$(^{Me}CC^{prop})] (**2**) as a greenish yellow solid, which is soluble in dmso, dmf, MeCN, and CH$_2$Cl$_2$, sparingly soluble in CHCl$_3$, MeOH, and EtOH, and insoluble in water, thf, hexane, diethyl ether, toluene, and ethyl acetate. The positive mode ESI mass spectrum of **2** is dominated by isotopic patterns centered at *m*/*z* = 393 and *m*/*z* = 363 for the monochelate fragments [NiOMe(^{Me}CC^{prop})]$^+$ and [Ni(^{Me}CC^{prop})]$^+$, respectively, which are due to loss of both bromido ligands in **2**. This fact corroborates the strong *trans* effect of the dibenzimidazolin-2-ylidene ligand. On the other hand, ions indicative of the bis(chelate) complexes have not been observed. The ^{1}H NMR spectrum in [D$_6$]dmso is rather simple and shows broad signals. Resonances at δ = 5.96 and 5.02 ppm for the NCH$_2$ and at δ = 2.73 and 1.95 ppm for the CH$_2$ groups are in accordance with the diastereotopy of the propylene-bridge protons upon coordination. The ^{13}C NMR spectroscopic data also supports the formation of **2**, although the carbenoid carbon atom could not be resolved under the given conditions despite prolonged acquisition times of >30000 scans of a saturated solution, which may be explained by the insufficient solubility of the complex.

To confirm the identity of **2**, we obtained single crystals by vapor diffusion of diethyl ether into a dmf solution of the complex, which were then subjected to X-ray diffraction analysis. The molecular structure of complex **2**[17] depicted in Figure 2 shows a square-planar Ni^{II} center coordinated by the *cis*-chelating dicarbene ligand and two bromido ligands, which balance the charges. As expected, the Ni–C$_{carbene}$ distances of 1.863(7) and 1.855(8) Å are shorter than those in bis(chelate) **1**. The Ni–Br bond lengths of 2.4149(11) and 2.4287(12) Å are substantially longer than those found in the diphosphane analogue [NiBr$_2$(dppe)] (2.3205–2.3419 Å),[18,19] which suggests a superior *trans* influence of the dibenzimidazolin-2-ylidene ligand over that of the dppe ligand. Relative to complex **1**, the dihedral angle between the carbene and the NiBr$_2$C$_2$ coordination planes are significantly larger (81.08° and 84.07°), because of the more flexible propylene bridge. The bite angle of the ligand, however, remains almost unchanged in the complexes with methylene to propylene linkers [86.6(2)° for **1** and 86.4(3)° for **2**]. This phenomenon has also been noted for Pd^{II} complexes of dibenzimidazolin-2-ylidenes.[20] The preference for the formation of monochelate **2** is possibly due to the lower stability of its eight-membered metallacycle than that of the six-membered metallacycle in bis(chelate) **1**.

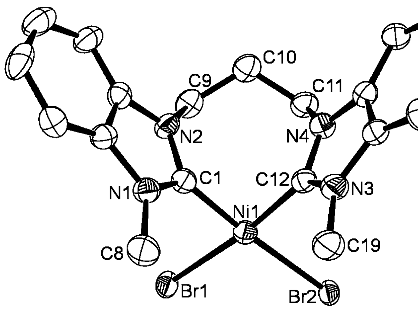


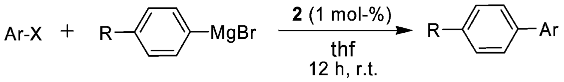
Figure 2. Molecular structure of the monochelate complex **2**·dmf showing 50% probability ellipsoids; hydrogen atoms and a dmf solvent molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C1 1.863(7), Ni1–C12 1.855(8), Ni1–Br1 2.4149(11), Ni1–Br2 2.4287(12), N1–C1 1.356(9), N2–C1 1.360(9), N3–C12 1.363(10), N4–C12 1.343(9); C1–Ni1–C12 86.4(3), C1–Ni1–Br1 87.9(2), C12–Ni1–Br2 88.5(2), Br1–Ni1–Br2 97.41(4), N1–C1–N2 106.4(6), N4–C12–N3 106.7(7).

With the successful isolation of monochelate **2**, we studied its possible autoionization behavior in solution. For this purpose a sample of **2** was dissolved in [D$_6$]dmso and monitored by ^{1}H NMR spectroscopy over 45 d. Only after about 10 d did new signals emerge, slowly gaining intensity until they became the major resonances after about 40 d. These signals are tentatively assigned to the dicationic bis(chelate) and some minor unidentified decomposition products. The positive mode ESI mass spectrum of this sample after 45 d shows a dicationic base peak at *m*/*z* = 333, which corroborates the formation of the bis(chelate) [Ni(^{Me}CC^{prop})$_2$]$^{2+}$. Isotopic patterns arising from **2**, on the other hand, were absent.

Kumada–Corriu Catalysis

Complexes of N-heterocyclic carbene ligands have been applied in both homogeneous and heterogeneous catalysis. In particular, Pd–NHC complexes have been widely used in the making of C–C bonds often by employing the Mizoroki–Heck and Suzuki–Miyaura coupling reactions. Similarly, some Ni–NHC complexes have shown to be catalytically active for a wide range of reactions such as Suzuki–Miyaura[21,22] and Kumada–Corriu[23–28] couplings, olefin dimerization[3] and polymerization,[29–32] C–C bond activation of biphenylene,[33] transfer hydrogenation of imines,[34] and amination[35] and dehalogenation[36] of aryl halides. Notably, most of these nickel complexes contain NHC ligands that are derived either from imidazole or imidazoline precursors, whereas the catalytic activity of Ni^{II}–benzimidazolin-2-ylidenes have rarely been studied.[5,22,28] Thus, complex **2** was tested for its performance in the nickel-catalyzed Kumada–Corriu reaction.[37] The coupling of aryl halides with arylmagnesium reagents at ambient temperature in thf with a 1 mol-% catalyst loading and a reaction time of 12 h was chosen as a standard test reaction. The results summarized in Table 1 show that **2** is generally very active in the coupling of both activated and deactivated aryl bromides and gives rise to isolated product yields of >70%. Simple aryl chlorides also afford satisfactory yields of 75 and 85%, respectively (Entries 9 and 10). Heteroaryl compounds such as 3-bromopyridine and 3-bromothiophene can also be conveniently coupled with yields of 78–85% (Entries 5, 6, 16, and 17). Likewise, 2,5-dibromopyridine affords the corresponding doubly coupled product in a good yield of 71% (Entry 7). Coupling of the sterically bulky and deactivated substrate 1-bromo-2,6-dimethoxybenzene turned out to be more difficult and gave a moderate yield of 58% (Entry 19). A similar result was also obtained with the more elaborate substrate 2-(4-bromophenyl)benzimidazole, which bears a N–H function (59%, Entry 20). Finally, the coupling of 2-chloropyridine gave the lowest yield of 43% in this comparative study (Entry 8). The catalytic activity of the previously reported *trans*-dibromido-bis(1,3-diisopropylbenzimidazolin-2-ylidene)nickel(II) complex[5] and the tetracarbene complex **1** was also tested in order to compare its performance to that of *cis*-chelating complex **2**. The *trans* complex couples bromobenzene, 4-bromobenzonitrile, and 4-bromoanisole with *p*-tolylMgBr in yields of 85, 63, and only 28%, respectively, whereas tetracarbene complex **1** performs slightly better to give yields of 88, 76 and 60%, respectively. Notably, complex **2** gave, in general, the best yields in analogous reactions (Entries 1, 3, 4, 11, 13, and 14). Finally, the catalytic activity of complex **2** with a *cis*-chelating benzannulated dicarbene ligand is also superior to that reported for a *trans*-dicarbene complex bearing monodentate imidazole-based NHC ligands.[25]

Table 1. Kumada–Corriu coupling reactions catalyzed by complex **2**.



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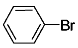
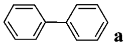
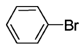
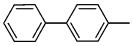
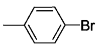
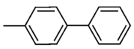
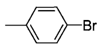
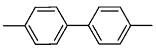
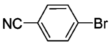
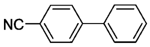
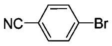
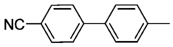
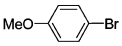
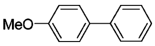
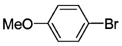
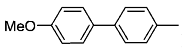
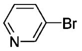
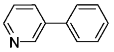
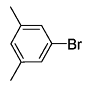
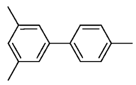
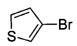
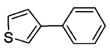
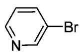
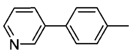
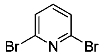
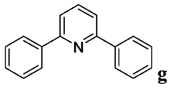
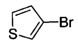
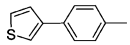
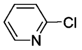
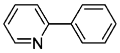
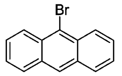
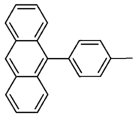
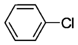
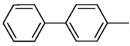
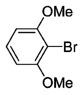
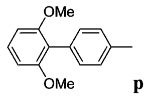
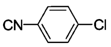
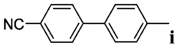
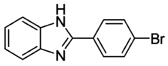
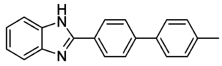
1		H	 **a**	>99	11		Me	 **b**	92
2		H	 **b**	91	12		Me	 **j**	>99
3		H	 **c**	89	13		Me	 **i**	83
4		H	 **d**	85	14		Me	 **k**	82
5		H	 **e**	78	15		Me	 **l**	81
6		H	 **f**	85	16		Me	 **m**	83
7		H	 **g**	71	17		Me	 **n**	88
8		H	 **h**	43	18		Me	 **o**	70
9		Me	 **b**	85	19		Me	 **p**	58
10		Me	 **i**	75	20		Me	 **q**	59

[a] Reaction conditions generally not optimized. [b] Isolated yields.

Conclusions

In conclusion, we have shown that the formation of bis(chelate) versus monochelate complexes can be determined by the bridge length of the chelating dicarbene ligand. The dicationic bis(chelate) complex $[\mathrm{Ni}(^{\mathrm{Me}}\mathrm{CC}^{\mathrm{meth}})_2]\mathrm{Br}_2$ (**1**) is exclusively formed with a rigid methylene spacer, whereas a more flexible propylene bridge favorably leads to the neutral monochelate species $[\mathrm{NiBr}_2(^{\mathrm{Me}}\mathrm{CC}^{\mathrm{prop}})]$ (**2**), which very slowly autoionizes to its corresponding bis(chelate) $[\mathrm{Ni}(^{\mathrm{Me}}\mathrm{CC}^{\mathrm{prop}})_2]^{2+}$ in [D$_6$]dmso solution. Complex **2** shows a high activity for the Kumada–Corriu coupling reaction of a wide range of substrates at ambient temperature and outperforms the *trans*-dicarbene complexes as well as tetracarbene complex **1**. The straightforward preparation and the low autoionization tendency of dicarbene complex **2** offers easy access to low-cost Ni^{II} dicarbene catalyst precursors, and current studies in our laboratory are underway to expand the scope of such complexes in catalysis.

Experimental Section

General: Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. Tetrahydrofuran for the Kumada–Corriu coupling reactions was dried with Na/benzophenone and freshly distilled prior to use. ^{1}H- and ^{13}C NMR spectra were recorded on Bruker ACF 300 and AMX 500 spectrophotometers, and the chemical shifts (δ) were internally referenced by the residual

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solvent signals relative to tetramethylsilane (^{1}H, ^{13}C). ESI mass spectra were measured with a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

[^{Me}CC^{prop}H$_2$]Br$_2$ (C): 1-methylbenzimidazole (0.66 g, 5 mmol) was dissolved in CH_3CN (30 mL). 1,3-dibromopropane (0.55 mL, 5.5 mmol) was added, and the resulting mixture was stirred for 24 h at 80 °C. The solvent was removed under reduced pressure, and the residue was washed with diethyl ether. After drying the residue under vacuum, salt **C** was isolated as a white powder (1.03 g, 2.21 mmol, 89 %). ^{1}H NMR (300 MHz, [D$_6$]dmso): δ = 9.92 (s, 2 H, NCHN), 8.13 (m, 2 H, Ar-H), 8.04 (m, 2 H, Ar-H), 7.70 (m, 4 H, Ar-H), 4.73 [t, ^3J(H,H) = 7.08 Hz, 4 H, NCH$_2$], 4.09 (s, 6 H, NCH$_3$), 2.62 [m, ^3J(H,H) = 7.08 Hz, 2 H, CH$_2$] ppm. ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]dmso): δ = 142.8 (s, NCN), 131.8, 130.8, 126.5, 126.4, 113.6, 113.5 (s, Ar-C), 43.8 (s, NCH$_3$), 33.3 (s, NCH$_2$), 28.1 (s, CH$_2$) ppm. $C_{19}H_{22}Br_2N_4{\cdot}2H_2O$ (502.24): calcd. C 45.44, H 5.22, N 11.16; found C 45.46, H 5.15, N 11.11. ESI-MS: *m/z* = 153 [M – 2Br]$^{2+}$.

[Ni(^{Me}CC^{meth})$_2$]Br$_2$ (1): Ni(OAc)$_2$ (0.026 g, 0.15 mmol), azolium salt **A** (0.072 g, 0.165 mmol), and [Bu$_4$N]Br (1 g, excess) were mixed thoroughly in a Schlenk tube. The reaction mixture was dried under vacuum at 80 °C for 1 h. The temperature was then gradually increased to 160 °C, and the molten mixture was further stirred for 12 h under vacuum. Cooling of the mixture and trituration with water gave a white precipitate, which was filtered and washed with water. Complex **1** was obtained as a white powder (0.046 g, 0.06 mmol, 80 %) upon drying under vacuum. ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 8.37 (d, 4 H, Ar-H), 7.69 (d, 4 H, Ar-H), 7.65 [d, ^2J(H,H) = 13.25 Hz, 2 H, NC*H*HN], 7.59 [d, ^2J(H,H) = 13.25 Hz, 2 H, NCH*H*N], 7.56 (t, 4 H, Ar-H), 7.47 (t, 4 H, Ar-H), 3.51 (s, 12 H, NCH$_3$) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]dmso): δ = 183.0 (NCN), 134.3, 133.1, 124.5, 124.2, 112.0, 111.2 (Ar-C), 57.0 (NCH$_2$N), 34.1 (NCH$_3$) ppm. Despite prolonged drying under vacuum, elemental analysis of the complex indicated the presence of water. $C_{34}H_{32}Br_2N_8Ni{\cdot}2H_2O$ (807.20): calcd. C 50.59, H 4.50, N 13.88.; found C 50.55, H 4.11, N 13.50. MS (ESI): *m/z* = 305 [M – 2Br]$^{2+}$, 691 [M – Br]$^+$.

[NiBr$_2$(^{Me}CC^{prop})] (2): Complex **2** was prepared in the same manner as that described for **1** with Ni(OAc)$_2$ (0.088 g, 0.5 mmol) and salt **C** (0.255 g, 0.55 mmol). Cooling of the molten mixture and trituration with water gave a yellowish green precipitate, which was filtered and washed with water. Complex **2** was obtained as a yellowish green powder (0.203 g, 0.39 mmol, 78 %) upon drying under vacuum. ^{1}H NMR (500 MHz, [D$_6$]dmso): δ = 7.58 (d, 4 H, Ar-H), 7.24 (br. s, 4 H, Ar-H), 5.96 (br. s, 2 H, NCH$_2$), 5.04 (br. s, 2 H, NCH$_2$), 4.59 (s, 6 H, NCH$_3$), 2.73 (br. s, 1 H, CH$_2$C*H*HCH$_2$), 1.95 (br. s, 1 H, CH$_2$CH*H*CH$_2$) ppm. ^{13}C{^{1}H} NMR (125.77 MHz, [D$_6$]dmso): δ = 134.5, 134.2, 122.9, 122.7, 110.3, 109.8 (Ar-C), 48.4 (NCH$_2$), 35.1 (NCH$_3$), 28.6 (CH$_2$CH$_2$CH$_2$) ppm. The carbenoid signal could not be resolved despite prolonged acquisition time. Despite prolonged drying under vacuum, elemental analysis of the complex indicated the presence of water. $C_{19}H_{20}Br_2N_4Ni{\cdot}H_2O$ (540.91): calcd. C 42.19, H 4.10, N 10.36.; found C 42.14, H 3.78, N 10.25. MS (ESI): *m/z* = 363 [M – 2Br]$^+$, 393 [M – 2Br + OCH$_3$]$^+$.

General Procedure for the Kumada–Corriu Coupling: In a typical run, a Schlenk tube was charged with catalyst **2** (0.01 mmol), aryl halide (1 mmol) (for Entry 7, 0.5 mmol). A thf solution of the arylmagnesium bromide (1.5 mL, 1 M, 1.5 mmol) was added to the reaction mixture under nitrogen. The reaction mixture was further stirred for 12 h at ambient temperature. Dichloromethane (10 mL) was added to the reaction mixture, and the organic layer was washed with water (3 × 10 mL) and dried with MgSO$_4$. The solvent was removed under reduced pressure, and the product was isolated by column chromatography and analyzed by ^{1}H NMR spectroscopy.

Single Crystal X-ray Structure Determinations: X-ray data were collected with a Bruker AXS SMART APEX diffractometer, by using Mo-K_α radiation at 223 K with the SMART suite of programs.[38] Data were processed and corrected for Lorentz and polarization effects with SAINT[39] and for absorption effects with SADABS.[40] Structural solution and refinement were carried out with the SHELXTL suite of programs.[41] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were placed at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in ref.[9] for **1** and ref.[12] for **2**. CCDC-695994 (for **1**·0.5H$_2$O), -695995 (for **2**·dmf) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ESI spectra for complexes **1** and **2** and analytical data for Kumada–Corriu coupling products are presented.

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[1] F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172.
[2] H. V. Huynh, J. H. H. Ho, T. C. Neo, L. L. Koh, *J. Organomet. Chem.* **2005**, *690*, 3854–3860.
[3] D. S. McGuinness, W. Mueller, P. Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White, U. Englert, *Organometallics* **2002**, *21*, 175–181.
[4] W. A. Herrmann, G. Gerstberger, M. Spiegler, *Organometallics* **1997**, *16*, 2209–2212.
[5] H. V. Huynh, L. R. Wong, P. S. Ng, *Organometallics* **2008**, *27*, 2231–2237.
[6] H. V. Huynh, C. Holtgrewe, T. Pape, L. L. Koh, E. Hahn, *Organometallics* **2006**, *25*, 245–249.
[7] W. A. Herrmann, J. Schwarz, M. G. Gardiner, M. Spiegler, *J. Organomet. Chem.* **1999**, *575*, 80–86.
[8] P. S. Jarrett, P. J. Sadler, *Inorg. Chem.* **1991**, *30*, 2098–2104.
[9] I. M. Angulo, E. Bouwman, M. Lutz, W. P. Mul, A. L. Spek, *Inorg. Chem.* **2001**, *40*, 2073–2082.
[10] M. V. Baker, B. W. Skelton, A. H. White, C. C. Williams, *J. Chem. Soc., Dalton Trans.* **2001**, 111–120.
[11] T. Scherg, S. K. Schneider, G. D. Frey, J. Schwarz, E. Herdtweck, W. A. Hermann, *Synlett* **2006**, *18*, 2894–2907.
[12] R. E. Douthwaite, D. Haüssinger, M. L. H. Green, P. J. Silcock, *Organometallics* **1999**, *18*, 4584–4590.
[13] Crystallographic details for **1**·0.5H$_2$O ($C_{34}H_{33}Br_2N_8NiO_{0.5}$): colorless rods, 0.24 × 0.06 × 0.04 mm, space group $P2_1/n$, monoclinic, a = 11.8792(15) Å, b = 10.0604(14) Å, c = 13.9968(19) Å, b = 97.895(4)°, V = 1656.9(4) Å^3, Z = 2, $\rho_{calcd.}$ = 1.564 mg/m^3, F(000)= 790, R(F) = 0.0877, Rw(F^2) = 0.1481, GOF = 1.141 [$I > 2\sigma(I)$].

[14] F. E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, *Angew. Chem. Int. Ed.* **2005**, *44*, 3759–3763.

[15] H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu, P. Y. Cheng, *Tetrahedron* **2004**, *60*, 5807–5825. Lee et al. could obtain ethylene-bridged Pd^{II} complexes only with benzylic N-substituents. However, these substituents were not included in this study so as to investigate the sole influence of the bridging unit.

[16] W. A. Herrmann, J. Schwarz, M. G. Gardiner, *Organometallics* **1999**, *18*, 4082–4089.

[17] Crystallographic details for **2**·dmf ($C_{22}H_{27}Br_2N_5NiO$): brown blocks, $0.16 \times 0.16 \times 0.10$ mm, space group $P2_12_12_1$, orthorhombic, $a = 8.1304(4)$ Å, $b = 15.8139(8)$ Å, $c = 18.7790(10)$ Å, $V = 2414.5(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.640$ mg/m^3, $F(000) = 1200$, $R(F) = 0.0619$, $Rw(F2) = 0.1444$, GOF = 1.143 [$I > 2\sigma(I)$].

[18] S. Beaudoin, D. Zargarian, F. Bélanger-Gariépy, F.-G. Fontaine, *Acta Crystallogr., Sect. E* **2001**, *57*, m433–m434.

[19] J. A. Rahn, A. Delian, J. H. Nelson, *Inorg. Chem.* **1989**, *28*, 215–217.

[20] F. E. Hahn, T. von Vehren, T. Lügger, *Inorg. Chim. Acta* **2005**, *358*, 4137–4144.

[21] D. S. McGuinness, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **1999**, *18*, 1596–1605.

[22] Z. Xi, X. Zhang, W. Chen, S. Fu, D. Wang, *Organometallics* **2007**, *26*, 6636–6642.

[23] V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2000**, *39*, 1602–1604.

[24] V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2001**, *40*, 3387–3389.

[25] K. Matsubara, K. Ueno, Y. Shibata, *Organometallics* **2006**, *25*, 3422–3427.

[26] J. Wolf, A. Labande, M. Natella, J.-C. Daran, R. Poli, *J. Mol. Catal. A* **2006**, *259*, 205–212.

[27] Y. Zhou, Z. Xi, W. Chen, D. Wang, *Organometallics* **2008**, *27*, 5911–5920.

[28] Z. Xi, B. Liu, W. Chen, *J. Org. Chem.* **2008**, *73*, 3954–3957.

[29] X. Wang, S. Liu, G.-X. Jin, *Organometallics* **2004**, *23*, 6002–6007.

[30] W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen, Y. Zhang, *Organometallics* **2005**, *24*, 5925–5928.

[31] B. E. Ketz, X. G. Ottenwaelder, R. M. Waymouth, *Chem. Commun.* **2005**, 5693–5695.

[32] J. Cámpora, L. O. de la Tabla, P. Palma, E. Álvarez, F. Lahoz, K. Mereiter, *Organometallics* **2006**, *25*, 3314–3316.

[33] T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *25*, 4196–4206.

[34] S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2003**, *22*, 4184–4186.

[35] B. Gradel, E. Brenner, R. Schneider, Y. Fort, *Tetrahedron Lett.* **2001**, *42*, 5689–5692.

[36] C. Desmarets, S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2002**, *21*, 1554–1559.

[37] Z.-X. Wang, L. Wang, *Chem. Commun.* **2007**, 2423–2425.

[38] *SMART version 5.628*, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

[39] *SAINT+ version 6.22a*, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

[40] G. W. Sheldrick, *SADABS version 2.10*, University of Göttingen, **2001**.

[41] *SHELXTL version 6.14*, Bruker AXS Inc., Madison, Wisconsin, USA, **2000**.

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