Synthesis of Pincer-type N-Heterocyclic Carbene Palladium Complexes with a Hemilabile Ligand and their Application in Cross-Coupling Catalysis

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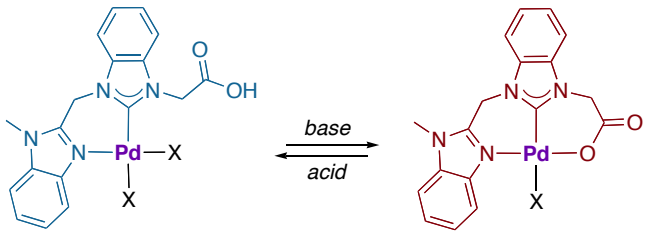
Abstract

Benzimidazolium salts containing both a neutral imine and a masked carboxylate functional group for potential metal chelation were prepared. Palladation of the ester-protected ligand afforded a *N,C*-bidentate carbene complex **4**. Subsequent ester hydrolysis preserved the bidentate coordination mode and yielded complex **5** with a pending COOH group exclusively. However, when ester deprotection was carried out prior to metalation, the *N,C,O*-tridentate pincer-type coordinated palladium complex **7** was obtained. Proton-abstraction of the dangling COOH group in the bidentate ligand of complex **5** by treatment with a base led to the formation of the *N,C,O*-tridentate coordinated Pd system **7**, and inversely, exposure of the tridentate bound Pd complex **7** with acid afforded the *N,C*-bidentate ligand coordination mode in complex **5**, demonstrating hemilability of the oxygen donor site in the pincer ligand. All three palladium(II) complexes **4**, **5**, and **7** were evaluated in cross-coupling catalysis and revealed distinct activity differences that are dependent on the type of coupling (Suzuki *vs.* Heck) and the substrate (Ar–Br vs. Ar–Cl). These differences suggest that judicious choice of donor groups in pincer-type complexes is a viable strategy for catalyst optimization.



active Suzuki catalytst with ArBr and ArCl
inactive Heck catalyst

active Suzuki catalytst with ArCl only
active Heck catalyst

1. Introduction

Organometallic pincer-type complexes featuring a M–C bond that is supported by different sets of chelating donor groups have found widespread application in catalysis [1]. Polydentate ligation enhances the stability of the metal-carbon bond and thus prevents metal leaching. In addition to the incorporation of classic N, P, S, and O-donor groups for chelation, N-heterocyclic carbenes (NHCs) [2] have become increasingly popular in the design of such pincer-type ligands over the last decade [3], in particular due to their exceptional success in transition metal catalysis [4] and beyond [5]. As strong σ donors that bind tightly to a broad range of (late) transition metal centers, NHCs are generally [6] useful spectator ligands to prevent complex decomposition [4]. The benefit of combining NHC ligands in a pincer ligand scaffold for metal coordination has been exploited with various types of NHC systems including for example imidazolylidenes [7], benzimidazolylidenes [8], pyridylidenes [9], and triazolylidenes [10].

While originally, pincer ligands were C2-symmetric and featured two identical donor sites in mutual *trans* position [11], recent work has increasingly focused on dissymmetric tridentate systems that combine ligating groups with different donor characteristics to support the M–C bond [12]. While neutral, soft [13] donors stabilize low-valent metal centers, anionic, hard donors in contrast enhance the stability of high-valent and electron-poor metals, and such bonding principles have recently started to emerge also with NHC complexes [14]. The design of ligands that possess both neutral and anionic donor sites may thus be of great benefit in catalytic applications for stabilizing critical transition states and for enabling concerted reaction pathways. Specifically, such a ligand design is expected to be advantageous for catalytic cycles that involve redox processes which require the accessibility of both high- and low-valent metal centers. Cross-coupling catalysis provides an attractive probe for this concept since stabilization of Pd^0 and Pd^{II} oxidation states is required for the Ar–X activation and the C–C bond forming steps, respectively [15]. While a few examples of NHC palladium complexes are known that contain both neutral and anionic donors (Figure 1) [16], only one of these complexes was investigated in catalysis. Complex **C** with a weakly coordinated sulfone ligand showed good activity in Suzuki-Miyaura cross-coupling reactions using aryl bromides as substrates [16c].

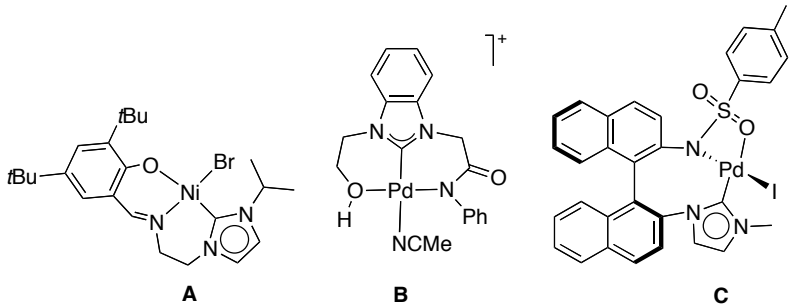


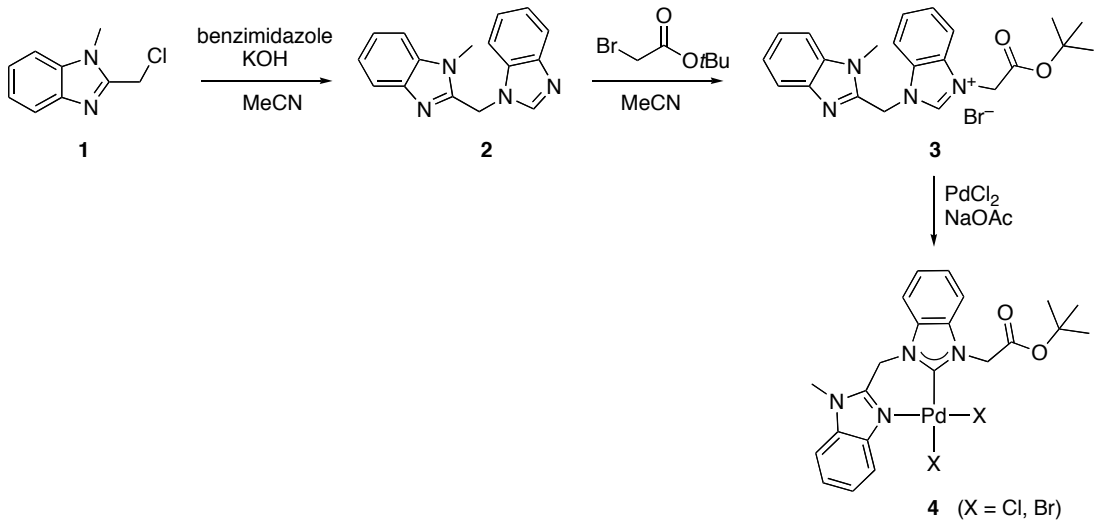
Figure 1 Pincer-type NHC complexes containing both anionic and neutral donors

Obviously, the concept has potential limitations. For example, if an already relatively stable intermediate is further stabilized, the catalytic turnover frequency will decrease and catalyst deactivation or even side reactions and irreversible catalyst decomposition pathways may become predominant. Cross-coupling reactions with different substrate-dependent, rate-determining steps are expected to provide insight into such decomposition pathways. Herein we report the synthesis of benzimidazolylidene palladium complexes with an ancillary neutral imine donor and a potentially chelating oxygen donor and their performance in Suzuki-Miyaura and Heck-type arylation of haloarenes and olefins, respectively.

2. Results and discussion

2.1 Synthesis and modification of ligand coordination modes

The synthetic route to the preparation of the benzimidazolium ligand is shown in Scheme 1. N-methyl-2-chloromethyl benzimidazole **1** was prepared via standard procedures [17], and reacted with benzimidazole in the presence of KOH to form **2** as a white crystalline solid. The formation of **2** was confirmed in the ^{1}H NMR spectrum by the emergence of a singlet at 7.99 ppm for the NC*H*N proton. Also, the presence of four new aromatic protons of equal integration for the new benzimidazole supported formation of **2**. The singlet for the CH_2 group shifted significantly downfield from 4.85 ppm in **1** to 5.65 ppm in **2**. Compound **2** was then reacted with *t*-butyl bromoacetate to give the azolium salt **3**. Upon formation of **3**, the compound was no longer soluble in $CDCl_3$. Formation of the azolium salt was indicated in the ^{1}H NMR spectrum by the new lowfield signal at 9.90 ppm for the acidic NC*H*N proton. Moreover a new singlet emerged at 1.49 ppm with correct integration for the nine protons of the *t*-butyl group.



Scheme 1 Synthesis of NHC palladium complex **4**

Complexation of **3** was initially attempted using Ag_2O and $PdCl_2$ in an *in-situ* transmetalation procedure. However, this reaction yielded mixtures of a monodentate and a bidentate complex as indicated by ^{1}H NMR spectroscopy and mass spectrometry. Metalation was then carried out using $PdCl_2$ and NaOAc in CH_3CN, which afforded the *N,C*-bidentate chelate complex **4** (Scheme 2). The product was identified by the loss of the acidic singlet at δ_H 9.90 ppm in the ^{1}H NMR spectrum, suggesting carbene coordination. The methyl groups of the BOC group shift from δ_H 1.49 ppm to 1.37 ppm upon palladation. Furthermore, all aromatic protons in **4** are slightly deshielded as compared to **3**. The CH_2 spacer groups appear as two sets of AB doublets at δ_H 6.37 and 6.08 ppm ($^2J_{HH}$ = 16.7 Hz), and at δ_H 5.79 and 5.58 ppm ($^2J_{HH}$ = 17.3 Hz). The different chemical environment of each methylene proton indicates chelation of the NHC ligand and/or rigid orientation of the NHC substituents. In the ^{13}C NMR spectrum the carbene carbon was detected at δ_C 166.6 ppm, which is typical of palladium-benzimidazolylidene complexes [8,18]. Upon complexation, the carbonyl carbon shifts significantly downfield from δ_C = 165.5 ppm to 176.0 ppm.

Unambiguous evidence for the formation of complex **4** was obtained by single crystal X-ray diffraction. Suitable crystals were obtained by diffusion of Et_2O into a $CHCl_3$ solution of the complex. Selected bond lengths and angles are compiled in Table 1. The molecular structure (Figure 2) features a square-planar palladium center with a *N,C*-bidentate chelating benzimidazole-benzimidazolylidene ligand. The Pd–C bond length is 1.9760(19), which is slightly longer than in related Pd-benzimidazolylidene complexes [19]. The complex crystallized with a 5:3 ratio of chlorides and bromides coordinated to the palladium center due to the presence of a Br^- counterion in the ligand and Cl^- ions in the metal precursor. From the

X-ray structure, the COO*t*Bu arm is in proximity to one of the halides bound to the metal center. Due to chelation of the NHC ligand, rotation about the N(4)-CH_2 bond is presumably limited. This steric restriction may rationalize the splitting of the ^{1}H NMR resonance of this CH_2 group into a AB doublet [20]. Accordingly, the AB pattern of a methylene signal is not per se evidence for chelation. Further evidence that the AB doublet is not associated with metal bonding was obtained from analysis of the carbonyl stretch vibration by IR spectroscopy. A band at 1740 cm^{-1} was observed both for the ligand precursor **3** and in the palladium complex **4**, indicating no significant perturbation of the ester group as would be expected from ester coordination.

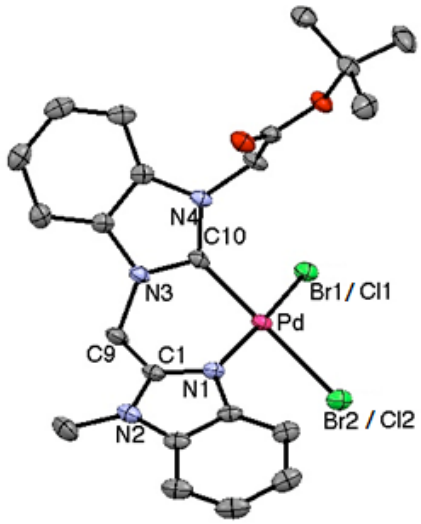


Figure 2 Ortep representation of **4** (50% probability level, hydrogen atoms omitted for clarity).

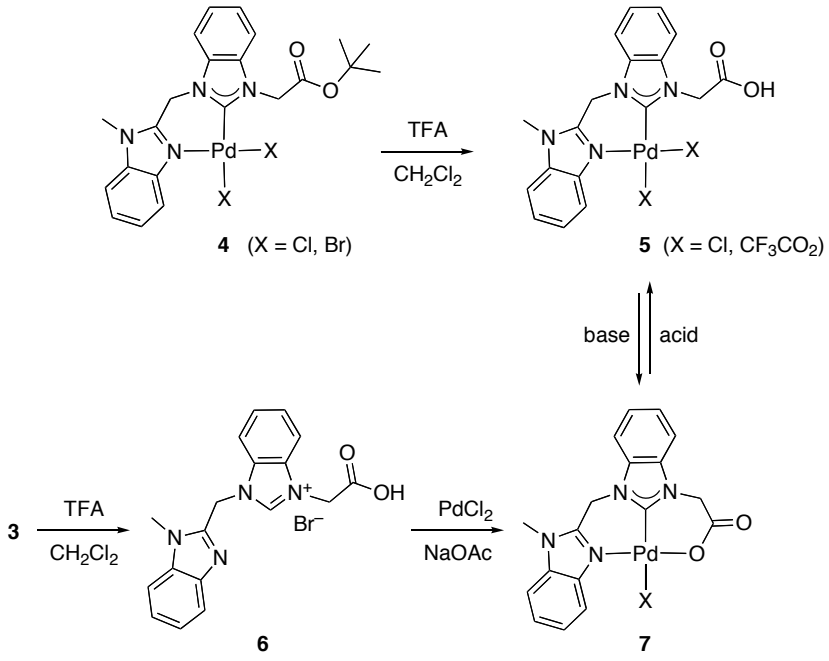
Table 1 Selected bond lengths (Å) and angles (°) in complex **4** [a)]

Pd-C10	1.9760(19)	C10-Pd-N1	86.72(7)
Pd-N1	2.0471(16)	C10-Pd-X1	91.48(5)
Pd-X1	2.3910(3)	N1-Pd-X1	170.55(5)
Pd-X2	2.4360(4)	C10-Pd-X2	178.37(5)
		N1-Pd-X2	94.29(5)
		X1-Pd-X2	87.32(12)

[a)] X1: 54% Cl, 46% Br; X2: 71% Cl, 29% Br

Deprotection of complex **4** with trifluoroacetic acid (TFA) resulted in the clean cleavage of the BOC group with no impact on the coordination of the ligand (Scheme 2). Complex **5** features only marginal shifts in the ^{1}H NMR spectrum compared to **4**. The most diagnostic change was the loss of the singlet at 1.37 ppm for the *t*-butyl group and a downfield shift of

one of the CH_2 AB signals (δ_H 6.19 and 5.96 ppm, $^2J_{HH}$ = 16.7 Hz). Since the higher field AB pattern is essentially unaffected, we tentatively attribute this latter signal to the CH_2 group interlinking the two benzimidazole fragments, and the former to the carbonyl-bound CH_2 entity. In the ^{13}C NMR spectrum of complex **5**, the carbene carbon resonance was observed at δ_C 168.6 ppm, slightly upfield as compared with the ester-functionalized carbene in complex **4**. While the carbonyl carbon signal appears at δ_H 174.0 ppm and hence almost the same frequency as in complex **4**, the shift of the CO band from ν_{CO} 1740 to 1678 cm^{-1} in the IR spectrum provides strong support for the formation of the carboxylic acid. According to microanalysis, the two anionic ligands are Cl^- and CF_3COO^-, the latter resulting from TFA-mediated BOC group cleavage.



Scheme 2 Synthesis of complexes **5** and **7** containing a pending or coordinated carboylate group, respectively.

Acid deprotection was also prerformed from the ligand precursor **3** prior to palladation, thus affording compound **6** in moderate yields. Noteworthy, the deprotection of the ligand proceeds in lower yields than the deprotection of the complex (48% vs. 78%). Upon palladation starting from the deprotected ligand **6**, the tridentate coordinated Pd complex **7** was obtained exclusively. Complex **7** was also prepared via transmetalation using Ag_2O and $PdCl_2$ as the transmetalating agent. Two equivalents of Ag_2O were needed to form the complex, whereas no metalation was observed when only one equivalent was used. This outcome is presumably due to the presence of two competing acidic sites for deprotonation,

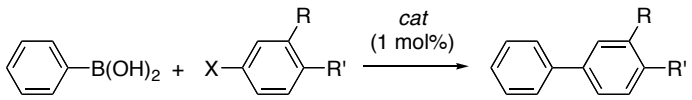
i.e. the carboxylic acid and the azolium proton. Complex **7** was characterized by ^{1}H NMR spectroscopy, which revealed the loss of the benzimidazolium proton at δ_H 9.92 ppm. The most noteworthy features in the ^{1}H NMR spectrum are the two singlets at δ_H 6.08 ppm and 5.08 ppm attributed to the two methylene linkers in complex **7**. The singlet multiplicity suggests either a molecular C_S symmetry due to completely planar coordination of the pincer ligand, or more likely for this type of ligands [21], fast puckering that involves wagging of the benzimidazolylidene ligand with respect to the C–Pd–X axis. Rapid interconversion of the two limiting conformations transforms pseudo-equatorial protons of the CH_2 linkers into pseudo-axial protons and vice versa. In agreement with such a puckered conformation, these two singlets are significantly broadened ($w_{1/2}$ = 5 and 6 Hz) as compared with the resonances due to those groups in the ligand precursor **6** ($w_{1/2}$ = 2 Hz), which may indicate dynamic processes upon complexation. The methyl singlet shifts downfield from δ_H 3.95 ppm in **6** to 4.00 ppm in the complex. The carbene carbon was observed at δ_C 156.3 ppm, which is considerably higher field than in complex **4** (δ_C 166.6 ppm). The carbonyl fragment is only marginally affected by the coordination of the carboxylate and shifts from δ_C 168.2 ppm in **6** to 168.6 ppm in **7**. This resonance is also at significantly higher field than that of complex **4** (δ_C 176.0 ppm). In IR spectroscopy, a broad signal at 1624 cm^{-1} was attributed to the C=O vibration and a sharper band at 1385 cm^{-1} for the C–O bond vibration, which is in agreement with reported values of coordinated carboxylates [22].

Coordination and dissociation of the *O*-donor in the pincer complexes **5** and **7** is pH-dependent. The addition of 1 equiv. of HCl (1 M solution) to complex **7** afforded the bidentate coordinated Pd complex **5** cleanly without further purification. Complex **5** was also formed with 1 equiv. HBr (1 M solution), however, other acids such as H_2SO_4 and CH_3COOH had no effect on **7**. This reactivity pattern is presumably due to the need of a strongly coordinating anion to displace the carboxylate donor group in combination with the stability of the chelate. Complex **7** was stable towards base. One equiv. NaOH (1 M) had no apparent effect on the complex, and only after the introduction of a large exess (>10 equiv.) decomposition started to be observed. The addition of 1 equiv. base such as NaOH, NaOAc and NEt_3 to the *N,C*-bidentately bound Pd complex **5** induced coordination of the carboxylate group and formation of the tridentate chelate **7**. These reactions were also scaled up and have been carried out on a 500 mg scale and demonstrate a flexible behavior of the pincer ligand and hemilabile coordination.

2.2 Cross-coupling catalysis

The palladium(II) complexes **4**, **5** and **7** were tested in the Suzuki-Miyaura coupling of deactivated aryl bromides (bromoanisole) and activated aryl chlorides (chlorobenzaldehyde) with phenylboronic acid at mild temperatures (50 °C, Table 2) [23]. Low temperatures were chosen to prevent the formation of colloidal particles as much as possible [24]. Under these conditions, the bidentate coordinated Pd complex **5** shows the highest activity with moderate to good conversions (Table 2, entries 2 and 5). Complex **7** with a tridentate ligand and the bidentate chelate **4** show both only low conversions for the coupling of 3-bromoanisole and phenylboronic acid (entries 1 and 3). Although weak bases are sufficient to transform **5** into **7**, such a reaction does not seem to be relevant under catalytic conditions when considering the distinct activities of these two complexes. Presumably, the preferred reaction of the base involves the phenylboronic acid rather than the carboxylic acid in **5**, thus inducing cross-coupling catalysis. Remarkably, superior activity of **5** over **7** was only observed for aryl bromide coupling. With aryl chlorides the tridentate coordinated Pd complex **7** is equally efficient as **5** and achieves similar conversions after 24 h (enteries 5 and 6), while the ester-functionalized NHC complex **4** displays lower activity. The different impact of bi- *vs*. tridentate coordination towards conversion of ArBr *vs*. ArCl may be correlated with the different rate-limiting steps depending on the halide in the ArX substrate [25]. Accordingly the increased activity of complex **7** may be rationalized by an acceleration of the oxidative addition step due to the presence of an anionic donor. In contrast, the presumably rate-limiting transmetalation step in ArBr conversion is disfavored with **7**, probably because of the lower availability of coordination sites available for transmetalation. In agreement with such a model, the flexibility of the ligand in complex **5** accommodates both, stabilization of low oxidation states for facilitating ArCl bond activation and hemilability to provide a free coordination site for transmetalation in the conversion of ArBr substrates.

Table 2 Catalytic Suzuki-Miyaura cross coupling[a)]



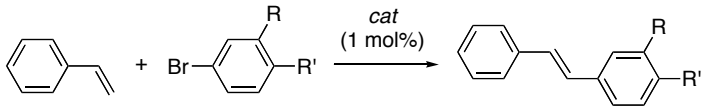
Entry	cat	X	R/R’	yield
1	**4**	Br	OMe/H	33%
2	**5**	Br	OMe/H	68%
3	**7**	Br	OMe/H	30%
4	**4**	Cl	H/CHO	40%

5	**5**	Cl	H/CHO	64%
6	**7**	Cl	H/CHO	57%

[a)] General reaction conditions: phenylboronic acid (1.2 mmol), Cs_2CO_3 (1.5 mmol), arylhalide (1.0 mmol) and complex **4**, **5**, **7** (1 mol%) in 2-propanol (3.0 mL) at 50°C for 2 h; NMR spectroscopic yields.

Complexes **4, 5** and **7** were also tested in the Mizoroki-Heck olefination of aryl bromides (Table 3) [26]. Higher efficiencies were obtained for substrates with a methoxy substituent in *para* rather than *meta* position. Highest conversions were obtained with the tridentate coordinated Pd complex **7** as catalyst precursor (entries 3 and 6). Complex **4** and **5** possessing only neutral donors gave similar conversions, which were substantially lower than those achieved with the tridentate chelate **7** (entries 1, 2, 4, and 5). Even though the general reaction conditions are mildly basic (NaOAc) and thus similar to those applied for the transformation of bidentate ligand in complex **5** into a tridentate system in complex **7**, the different productivity of these two complexes implies that the catalytically active species are different. This difference is worth noting since unlike Suzuki-Miyaura cross-coupling reactions, Mizoroki-Heck olefination does not feature an acidic substrate for capturing the added base. Potentially, the carboxylic acid wingtip group in **5** may change the proton transfer (pH), thus accounting for the low conversion. Alternatively, the presence of HOAc as the product from chelation of the carboxylate when starting with complex **5** may induce non-productive side reactions such as hydro-dehalogenation. Attempts to improve catalysis by abstracting the chloride ligand in complex **7** with $AgBF_4$ only gave catalytically inactive species and no product formation was observed even after 24 h. This result may be due to the formation of a bimetallic system [27].

Table 3 Catalytic Mizoroki-Heck cross coupling[a)]



Entry	catalyst	X	R/R’	yield
a	**4**	Br	OMe/H	5%
b	**5**	Br	OMe/H	5%
c	**7**	Br	OMe/H	20%
d	**4**	Br	H/OMe	30%
e	**5**	Br	H/OMe	28%

f	**7**	Br	H/OMe	60%

[a)] General reaction conditions: styrene (560 μmol), NaOAc (440 μmol), bromoanisole (400 μmol) and palladium complex (1 mol%) in DMA (3.0 mL) at 50°C, 2 h; NMR spectroscopic yield.

3. Conclusion

Novel chelating benzimidazolylidene palladium(II) complexes were prepared and fully characterized. A rigidly *N,C*-bidentate coordinated Pd complex was obtained upon metalation of an ester-functionalized ligand. Facile deprotection yielded a bidentate chelate with a non-coordinating acid wingtip group. In contrast, complexation of the deprotected ligand formed a pincer-type *N,C,O*-tridentate coordinated Pd complex comprising a neutral imine and an anionic carboxylate donor. Coordination and decoordination of this carboxylate group is triggered by the addition of base and acid, respectively. The complexes show distinctly different activities in cross coupling reactions. The low activity of the rigidly bidentate system suggests that the presence of a potentially coordinating carboxylate is beneficial for cross coupling. Depending on the substrate and the type of coupling, catalytic performance increases when the carboxylate is dangling or coordinated. The presence of different types of donor sites (neutral and ionic) therefore constitutes an attractive concept for tailoring catalysts in non-isohypsic processes such as cross-coupling reactions and oxidation reactions.

4. Experimental

4.1 General comments

N-methyl-1-chloromethylbenzimidazole was prepared via reported procedures [17]. All other starting materials and reagents were obtained from commercial sources and were used as received unless otherwise stated. NMR spectra were recorded on Varian spectrometers operating at 400 or 500 MHz. Chemical shifts are reported in δ (ppm) relative to internal Me_4Si in $CDCl_3$ or residual protio solvents. ^{13}C NMR signals were assigned with the aid of two-dimensional cross-coupling experiments. For NMR assignments, bimi refers to the 1,3-disubstituted benzimidazole and Me-bimi refers to 1-methyl-2-substituted benzimidazole. IR spectra were obtained on a FTIR spectrometer, and are reported here in units of cm^{-1}. Elemental analysis was performed on an Exeter Analytical CE440 elemental analyzer. High-resolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray source.

4.2 Synthetic procedures

Synthesis of 2. A mixture of **1** (1.8 g, 10 mmol), benzimidazole (1.18 mg, 10 mmol) and finely ground KOH (672 mg, 12 mmol) was stirred at reflux in CH_3CN (50 mL) for 48 h. After solvent evaporation the crude solid was dissolved in CH_2Cl_2 (200 mL) and washed with 1 M KOH (aq.) (3 x 50 mL), brine (50 mL) and dried over $MgSO_4$. After solvent evaporation the residue was purified by column chromatography (SiO_2, CH_2Cl_2 : MeOH 8:2), or using the KP-NH Biotage columns with 100% ethyl acetate to provide **2** (1.62 g, 62%) as white microcrystalline powder.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99 (s, 1H, NCHN), 7.83–7.80 (m, 2H, $CH_{Me\text{-}bimi}$, CH_{bimi}), 7.49 (d, 1H, $^3J_{HH}$ = 8.8 Hz, CH_{bimi}), 7.33–7.26 (m, 5H, 3 $CH_{Me\text{-}bimi}$, 2 CH_{bimi}), 5.65 (s, 2H, CH_2), 3.58 (s, 3H, CH_3). ^{13}C{H} NMR ($CDCl_3$, 100 MH_Z): δ = 147.4 (NCN), 144.0 (C_{bimi}), 142.3 (C_{bimi}), 142.2 ($C_{Me\text{-}bimi}$), 136.3 ($C_{Me\text{-}bimi}$), 133.8 (C_{bimi}), 123.8 ($C_{Me\text{-}bimi}$, $CH_{Me\text{-}bimi}$, CH_{bimi}), 122.9 ($CH_{Me\text{-}bimi}$), 122.8 (C_{bimi}, CH_{bimi}), 120.8 (CH_{bimi}), 120.4 ($CH_{Me\text{-}bimi}$), 109.6 ($CH_{Me\text{-}bimi}$), 110.2 (CH_{bimi}), 42.8 (CH_2), 30.2 (CH_3). Elemental analysis calcd. for $C_{15}H_{11}N_4$ (262.3): C 73.26, H 5.38, N 21.36; found: C 73.23, H 5.41, N 21.38. HR-MS (m/z): 263.1284, calcd for $[M+H]^+$ 263.1297.

Synthesis of 3. A mixture of **2** (1.63 g, 6.2 mmol) and *t*-butyl bromoacetate (0.9 mL, 6.2 mmol) was refluxed in CH_3CN (15 mL) for 24 h. The solvent was reduced to about 5 mL and the product was precipitated from Et_2O (50 mL). Repeated precipitation from CH_2Cl_2/Et_2O afforded product **3** as a white solid (1.5 g, 53%).

^{1}H NMR (DMSO–D_6, 400 MHz): δ = 9.90 (s, 1H, NCHN), 8.11–8.08 (m, 2H, H_{bimi}), 7.76–7.69 (m, 2H, H_{bimi}), 7.67 (d, 1H, $^3J_{HH}$ = 8.0 Hz, $H_{Me\text{-}bimi}$), 7.65 (d, 1H, $^3J_{HH}$ = 8.0 Hz, $H_{Me\text{-}bimi}$), 7.31 (t, 1H, $^3J_{HH}$ = 7.3 Hz, $H_{Me\text{-}bimi}$), 7.20 (t, 1H, $^3J_{HH}$ = 7.3 Hz, $H_{Me\text{-}bimi}$), 6.34 (s, 2H, CH_2), 5.62 (s, 2H, CH_2), 3.97 (s, 3H, CH_3), 1.49 (s, 9H, 3 × CH_3). ^{13}C{H} NMR (DMSO–D_6, 100 MHz): δ = 165.5 (C=O), 147.8 (NCN), 144.2 (NCHN), 141.5 ($C_{Me\text{-}bimi}$), 136.2 ($C_{Me\text{-}bimi}$), 131.4 (C_{bimi}), 131.2 (C_{bimi}), 127.0 (CH_{bimi}), 126.9 (CH_{bimi}), 122.8 (CH_{bimi}), 122.0 ($CH_{Me\text{-}bimi}$), 118.9 (CH_{bimi}), 114.2 ($CH_{Me\text{-}bimi}$), 113.9 ($CH_{Me\text{-}bimi}$), 110.4 ($CH_{Me\text{-}bimi}$), 83.3 (CMe_3), 48.2 (CH_2), 43.5 (CH_2), 30.1 (CH_3), 27.7 (CH_3). Elemental analysis calcd. for $C_{22}H_{25}N_4O_2Br$ (456.11) × 0.5 CH_2Cl_2: C 54.07, H 5.24, N 11.21; found: C 53.83, H 5.34, N 11.09. HR-MS (m/z): 377.1995, calcd for $[M–Br]^+$ 377.1977. IR: (CO) 1740 cm^{-1}.

Synthesis of 4. A mixture of **3** (1.5 g, 3.63 mmol), NaOAc (0.04 g, 4.87 mmol) and $PdCl_2$ (0.60 g, 0.32 mmol) was refluxed in CH_3CN (20 mL) for 24 h. The solution was filtered through a pad of Celite and the solvent reduced to 5 mL. Et_2O (25 mL) was added which

precipitated the product as a yellow powder. The residue was purified by flash column chromatography (SiO_2, CH_2Cl_2/CH_3CN 1:9). Crystals were grown by diffusion of Et_2O into a solution of **4** dissolved in $CHCl_3$ (1.0 g, 50%).

^{1}H NMR (DMSO–D_6, 500 MHz): δ =8.31 (d, 1H, $^3J_{HH}$ = 8.1 Hz, $H_{Me\text{-}bimi}$), 8.14 (d, 1H, $^3J_{HH}$ = 8.1 Hz, $H_{Me\text{-}bimi}$), 7.68 (d, 1H, $^3J_{HH}$ = 8.1 Hz, H_{bimi}), 7.65 (d, 1H, $^3J_{HH}$ = 8.1 Hz, H_{bimi}), 7.47 (t, 1H, $^3J_{HH}$ = 7.5 Hz, $H_{Me\text{-}bimi}$), 7.41 (t, 1H, $^3J_{HH}$ = 7.5 Hz, H_{bimi}), 7.37 (t, 1H, $^3J_{HH}$ = 7.5 Hz, $H_{Me\text{-}bimi}$), 7.32 (t, 1H, $^3J_{HH}$ = 8.0 Hz, H_{bimi}), 6.37 (d, 1H, $^2J_{HH}$ = 16.7 Hz, CH_2), 6.08 (d, 1H, $^2J_{HH}$ = 16.7 Hz, CH_2), 5.79 (d, 1H, $^2J_{HH}$ = 17.3 Hz, CH_2), 5.58 (d, 1H, $^2J_{HH}$ = 17.3 Hz, CH_2), 4.09 (s, 3H, CH_3), 1.37 (s, 9H, 3 × CH_3). ^{13}C{H} NMR (DMSO–D_6, 125.5 MHz): δ = 176.0 (C=O), 166.6 (C-NHC), 148.4 ($C_{Me\text{-}bimi}$), 138.8 (C_{bimi}), 134.1 (C_{bimi}), 133.8 ($C_{Me\text{-}bimi}$), 132.8 (NCN), 124.2 (CH_{bimi}), 124.1 (CH_{bimi}),123.1 ($CH_{Me\text{-}bimi}$), 119.9 (CH_{bimi}), 112.0 ($CH_{Me\text{-}bimi}$), 111.8 ($CH_{Me\text{-}bimi}$), 111.7 ($CH_{Me\text{-}bimi}$), 109.6 (CH_{bimi}), 49.0 (CH_2), 42.7 (CH_2), 31.5 (CH_3), 27.2 (3 × CH_3). Elemental analysis calcd. for $C_{22}H_{24}Br_2N_4O_2Pd$ (692.68): C 41.11, H 3.76, N 8.72; found: C 41.93, H 3.63, N 8.83. IR: (CO) 1740 cm^{-1}.

Synthesis of 5. Complex **4** (0.1 g, 0.2 mmol) was dissolved in CH_2Cl_2 (10 mL). TFA (0.1 mL, 2 mmol) was added dropwise in an ice bath. The solution was allowed to warm to room temperature and stirred for 4 h. Et_2O (30 mL) was added to precipitate the product **5** as a brown solid. The residue was purified by flash column chromatography (SiO_2, CH_2Cl_2/CH_3CN 1:9) to yield **5** as an off-white solid (0.07 g, 78%)

^{1}H NMR (DMSO–D_6, 500 MHz): δ = 8.11 (d, 1H, $^3J_{HH}$ = 8.3 Hz, $H_{Me\text{-}bimi}$), 8.03 (d, 1H, $^3J_{HH}$ = 7.8 Hz, $H_{Me\text{-}bimi}$), 7.63 (d, 1H, $^3J_{HH}$ = 7.3 Hz, H_{bimi}), 7.58 (d, 1H, $^3J_{HH}$ = 8.6 Hz, H_{bimi}), 7.45 (t, 1H, $^3J_{HH}$ = 8.3 Hz, $H_{Me\text{-}bimi}$), 7.45 (m, 2H, H_{bimi}), 7.33 (t, 1H, $^3J_{HH}$ = 7.8 Hz, $H_{Me\text{-}bimi}$), 6.19 (d, 1H, $^2J_{HH}$ = 16.6 Hz, CH_2), 5.96 (d, 1H, $^2J_{HH}$ = 16.6 Hz, CH_2), 5.83 (d, 1H, $^2J_{HH}$ = 18.5 Hz, CH_2), 5.50 (d, 1H, $^2J_{HH}$ = 18.5 Hz, CH_2), 4.02 (s, 3H, CH_3). ^{13}C{H} NMR (DMSO–D_6, 125.5 MHz): δ = 174.0 (C=O), 168.6 (C-NHC), 148.8 ($C_{Me\text{-}bimi}$), 137.4 (C_{bimi}), 134.5 (C_{bimi}), 133.7 ($C_{Me\text{-}bimi}$), 132.4 (NCN), 123.4 (CH_{bimi}), 123.3 (CH_{bimi}), 120.6 ($CH_{Me\text{-}bimi}$), 120.1(CH_{bimi}), 113.8 ($CH_{Me\text{-}bimi}$), 112.9 ($CH_{Me\text{-}bimi}$), 112.5 ($CH_{Me\text{-}bimi}$), 112.0(CH_{bimi}), 50.7 (CH_2), 43.4 (CH_2), 32.0 (CH_3). Elemental analysis calcd. for $C_{20}H_{16}ClF_3N_4O_4Pd$ (573.98) × 0.5 CH_2Cl_2: C 39.86, H 2.77, N 9.07; found: C 39.84, H 3.07, N 8.90. HR-MS (m/z): 460.9839, calcd for $[M–TFA]^+$ 460.9996. IR: 1678 cm^{-1}.

Synthesis of 6. Compound **3** (0.5 g, 1 mmol) was dissolved in CH_2Cl_2 (10 mL) in an ice bath. Trifluoroacetic acid (3.5 mL, 43 mmol) was added dropwise to the solution, which was left

stirring for 16 h. The solvent was removed and the product was re-dissolved in CH_2Cl_2 (5 mL) and precipitated from Et_2O (100 mL) to afford product **6** as a white solid (0.27 g, 48%). ^{1}H NMR (DMSO–D_6, 400 MHz): 9.92 (s, 1H, NCHN), 8.08–8.06 (m, 2H, CH_{bimi}), 7.79–7.67 (m, 2H, CH_{bimi}), 7.65 (d, 1H, $^3J_{HH}$ = 8.2 Hz, $CH_{Me\text{-}bimi}$), 7.53 (d, 1H, $^3J_{HH}$ = 8.2 Hz, $CH_{Me\text{-}bimi}$), 7.31 (t, 1H, $^3J_{HH}$ = 7.2 Hz, $CH_{Me\text{-}bimi}$), 7.22 (t, 1H, $^3J_{HH}$ = 7.2 Hz, $CH_{Me\text{-}bimi}$), 6.31 (s, 2H, CH_2), 5.57 (s, 2H, CH_2), 3.95 (s, 3H, CH_3). ^{13}C{H} NMR (DMSO–D_6, 100 MHz): δ = 168.2 (C=O), 147.9 (NCN), 144.5 (NCHN), 141.0 ($C_{Me\text{-}bimi}$), 136.6 ($C_{Me\text{-}bimi}$), 131.9 (C_{bimi}), 131.5 (C_{bimi}), 127.4 (CH_{bimi}), 127.3 (CH_{bimi}), 123.5 ($CH_{Me\text{-}bimi}$), 122.8 (CH_{bimi}), 119.0 ($CH_{Me\text{-}bimi}$), 114.4 (CH_{bimi}), 114.3 (CH_{bimi}), 110.0 ($CH_{Me\text{-}bimi}$), 48.1 (CH_2), 43.6 (CH_2), 30.6 (CH_3). Elemental analysis calcd. for $C_{18}H_{17}N_4O_2Br$ (322.14) × 0.25 CH_2Cl_2 × 0.25 Et_2O: C 52.53, H 4.07, N 12.71; found: C 52.43, H 4.57, N 12.70. HR-MS (m/z): 321.1346, calcd for $[M–Br]^+$ 321.1351. IR: (CO) 1741 cm^{-1}.

Synthesis of 7. Complex **7** was prepared using the same procedure as for **4** but starting from ligand **6** (1.0 g, 2.4 mmol), NaOAc (0.26 g, 3.2 mmol) and $PdCl_2$ (0.42 g, 2.4 mmol). Complex **7** was obtained as a yellow powder (0.70 g, 63%).
^{1}H NMR (DMSO–D_6, 500 MHz): δ = 8.43 (d, 1H, $^3J_{HH}$ = 8.2 Hz, $CH_{Me\text{-}bimi}$), 8.19 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{bimi}), 7.82 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{bimi}), 7.65 (d, 1H, $^3J_{HH}$ = 8.2 Hz, $CH_{Me\text{-}bimi}$), 7.42 (t, 1H, $^3J_{HH}$ = 7.4 Hz, CH_{bimi}), 7.39 (t, 1H, $^3J_{HH}$ = 7.8 Hz, CH_{bimi}), 7.33 (t, 1H, $^3J_{HH}$ = 7.4 Hz, $CH_{Me\text{-}bimi}$), 7.23 (t, 1H, $^3J_{HH}$ = 7.8 Hz, $CH_{Me\text{-}bimi}$), 6.08 (s, 2H, CH_2), 5.08 (s, 2H, CH_2), 4.00 (s, 3H, CH_3). ^{13}C{H} NMR (DMSO–D_6, 125.5 MH_Z): δ = 168.6 (C=O), 156.3 (C_{carb}), 148.0, 134.4, 134.2 (3 × $C_{Me\text{-}bimi}$), 132.6, 124.6 (2 × C_{bimi}), 124.4, 124.3, 124.1, 122.7 (4 × $CH_{Me\text{-}bimi}$), 112.5, 112.4, 112.2, 120.5 (4 × CH_{bimi}), 50.9 (CH_2), 43.4 (CH_2), 32.1 (CH_3). Elemental analysis calcd. for $C_{18}H_{15}ClN_4O_2Pd$ (459.99) × CH_2Cl_2: C 41.78, H 3.14, N 10.26; found: C 41.82, H 3.27, N 9.48. Despite repetitive precipitations, the %N remained too high. HR-MS (m/z): 458.9748, calculated for $[M–H]^+$ 458.9840. IR: 1624 cm^{-1}.

4.3 Representative catalytic procedures

Suzuki cross coupling catalysis: Catalyst (1 mol%), phenylboronic acid (147 mg, 1.2 mmol), Cs_2CO_3 (0.48 g, 1.5 mmol), 4-chlorobenzaldehyde or 3-bromoanisole (1.0 mmol), 2-propanol (3 mL) were added to a schlenk flask equipped with magnetic stirrer. The mixture was placed in a pre-heated oil bath at 50 °C for 24 h. The mixture was quenched with H_2O (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated in vacuo.

Heck cross coupling catalysis: Catalyst (1 mol%), styrene (64 μL, 560 μmol), NaOAc (36 mg, 440 μmol), bromoanisole (400 μmol), and DMA (3 mL) were added to a schlenk flask equipped with magnetic stirrer. The reaction mixture was placed in a pre-heated oil bath at 110 °C for 24 h. The mixture was quenched with H_2O (25 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated in vacuo.

4.4 Crystallographic details

Crystal data for **4** were collected using an Agilent Technologies SuperNova A diffractometer fitted with an Atlas detector and using monochromated Mo–K_α radiation (0.71073 Å). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical numeric absorption correction was performed [24]. The structure was solved by direct methods using SHELXS-97 [29] and refined by full matrix least-squares on F^2 for all data using SHELXL-97 [29]. Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl groups) the equivalent one of the parent atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. Disordered solvent was treated with the SQUEEZE procedure as implemented in PLATON [30]. Further crystallographic details are compiled in Table 4. CCDC number 999440 contains 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.

Table 4 Crystallographic data for complex **4**

Crystal size / mm	0.12 × 0.08 × 0.05
Empirical formula	$C_{23.50}\ H_{27.25}\ N_{4.25}\ O_{2.25}\ Cl_{1.25}\ Br_{0.75}\ Pd$
Fw	615.84
T /K	100(2)
Crystal system	Triclinic
Space group	P–1 (#2)
Unit cell	
a /Å	10.08185(8)
b /Å	10.54498(11)
c /Å	13.42923(16)
α /°	74.1843(9)
β /°	71.6551(9)
γ /°	89.8778(7)
Volume /Å^3	1298.36(2)
Z	2
D_{calcd} /g cm^{-3}	1.575
μ /mm^{-1}	2.024
F(000)	619

Reflections collected / R(int)	23543 / 0.0243
Max. and min. transmission	0.968 – 0.928
Data / restraints / parameters	6444 / 0 / 286
Goodness–of–fit on F^2	1.073
Final R indices for I>2σ(I)	R1 = 0.0241, wR2 = 0.0624
R indices for all data	R1 = 0.0285, wR2 = 0.0642
Largest diff. peak, hole /e Å^{-3}	0.479, –0.470

5. Acknowledgement

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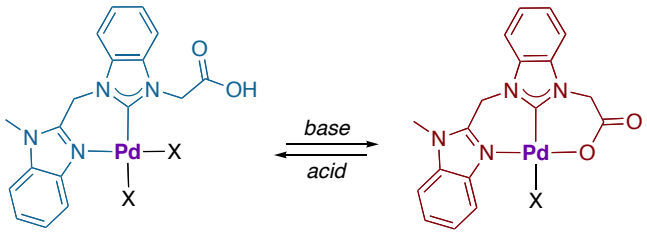
Highlights

- Pincer type N,C,O-tridentate carbene palladium complexes were synthesized
- Hemilabile O-donor site binding and dissociation is demonstrated
- Catalytic activity in cross-coupling depends on the ligand coordination mode

Graphical Synopsis



active Suzuki catalytst with ArBr and ArCl
inactive Heck catalyst

active Suzuki catalytst with ArCl only
active Heck catalyst

Pincer-type N-heterocyclic carbene palladium complexes featuring a *N,C,O*-tridentate ligand with a hemilabile oxygen donor display diverging catalytic activity that is in parts controlled by the (de)coordination of the oxygen donor.