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A Novel Pyridine-Bridged Bis-benzimidazolylidene Pincer Palladium Complex: Synthesis and Catalytic Properties

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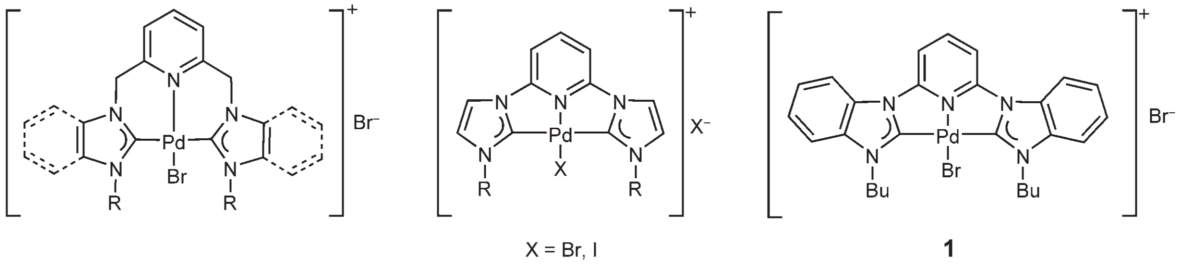
Dedicated to Professor R. W. Hoffmann on the occasion of his 75th birthday.

Abstract: A novel pyridine-bridged bis-benzimidazolylidene CNC pincer complex **1** was synthesized from cheap, commercially available precursors under microwave assistance in moderate yield. It catalyzes cross-coupling reactions of aryl halides with alkyl acrylates (Heck reaction) and phenylboronic acid (Suzuki reaction) under aerobic conditions with extremely high turn-over numbers (frequencies) indicating that a planar extension of the π-system by benzannelation significantly increases the catalytic activity even with trace amounts of catalyst loading.

Keywords: benzimidazoles; carbenes; Heck reaction; palladium; Suzuki coupling

Currently, organometallic pincer complexes attract much attention because of their widespread applications in catalysis and material sciences.[1] Compared with phosphine ligands, N-heterocyclic carbene (NHC) ligands act as stronger σ-donors and weaker π-acceptors[2] which increases electronic density at the metal center and improves the catalytic activity. Moreover, the stable carbon-metal bonds impose a higher stability of pincer carbene complexes against oxygen, moisture and heat.[3]

Pyridine- and lutidine-bridged CNC pincer carbene complexes bearing two fused metallacycles (Scheme 1) have been developed to efficient catalysts for homogenous C–C and C–N coupling reactions and olefin metathesis.[2–4] Beside palladium complexes, related iron,[5] nickel,[6] cobalt,[5c,7] ruthenium[8] and chromium[5c,9] CNC pincer complexes have been studied. Recently, we reported that bis-imidazolylidene palladium pincer complexes efficiently gelate a variety of organic solvents even in very low concentration, and this type of complexes has been applied to the catalytic Michael addition in the gel state.[10a] Compared to imidazolylidenes, benzimidazolylidenes behave quite differently;[11] we speculated that their extended π-system and increased σ-donor properties may facilitate the synthesis of novel CNC pincer complexes revealing higher catalytic activities and specific material properties. For example, lutidine-bridged bis-benzimidazolylidene pincer complexes have been successfully applied to Heck reactions even with less active bromobenzenes.[3c] Following our recent interest in the development of novel organometallics and their application in catalysis and soft matter,[10,12] we designed pyridine-bridged bis-benzimidazolylidene pincer complexes.

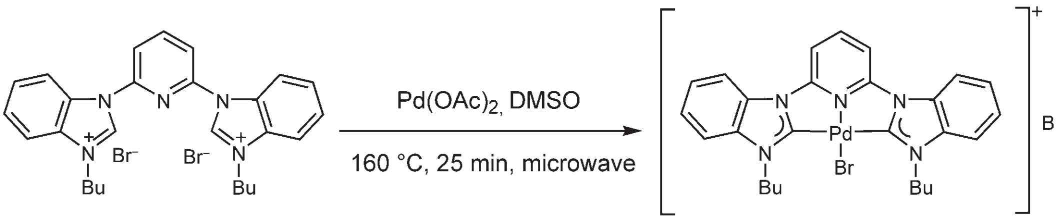


Scheme 1. Lutidine- and pyridine-bridged CNC pincer palladium carbene complexes.

Palladium pincer complex **1** is easily accessible in moderate yield by microwave-assisted palladation of the corresponding pyridine-bridged bis-benzimidazolium bromide **2** with $Pd(OAc)_2$ (Scheme 2). Bis-benzimidazolium bromide **2** was synthesized by amination of 2,6-difluoropyridine with 2 equivalents of benzimidazole followed by *N*-alkylation with butyl bromide in a sealed tube. In contrast to its imidazolylidene bromo analogues,[4c] the bis-benzimidazolylidene pincer palladium complex **1** is readily soluble in CH_2Cl_2, even though its extended planar π-system is expected to favour intermolecular stacking.

As part of our effort to demonstrate the utility of novel metal carbenes in catalysis and material sciences,[10] we explored the catalytic properties of bis-NHC pincer palladium complex **1** in the Heck reaction of aromatic halides and alkyl acrylates. The reactions were performed under aerobic conditions in 1-methyl-2-piperidone (NMP) at 140 °C demonstrating the resistance of carbene complex **1** against air, moisture and heat (Table 1). A 0.2 mol% catalyst loading turned out to be sufficient for the coupling of iodobenzene with butyl acrylate within 8 h in good to quantitative yields using a selection of organic and inorganic bases (Table 1, entries 1–4). Similarly, the coupling of the less reactive bromobenzene resulted in an almost quantitative yield under these conditions (Table 1, entry 5); chlorobenzene, however, afforded only trace amounts of **3a** even after the reaction time had been extended to 24 h.

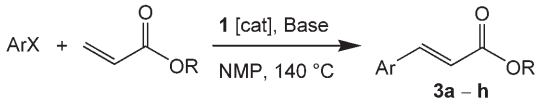
In order to investigate the influences of electronic and steric properties of the substrates, a variety of aryl halides were studied in model reactions using butyl acrylate and K_2CO_3 under our standard conditions in which the catalyst loading was decreased to 10^{-4} mol% Pd. Under these conditions, iodobenzene still afforded a 94% isolated yield of **3a** after 24 h (Table 1, entry 6) which, however, decreased to 27%



2 **1**

Scheme 2. Synthesis of pyridine-bridged bis-benzimidazolylidene pincer palladium complex **1**.

Table 1. Heck reaction of aryl halides and alkyl acrylates catalyzed by CNC pincer palladium complex **1**.[a]



Entry	ArX	R	Catalyst [mol%]	Base	Time [h]	Product	Yield [%][b]	TON
1	Iodobenzene	Bu	0.2	TEA	8	**3a**	98	495
2	Iodobenzene	Bu	0.2	*i*-Pr_2NEt	8	**3a**	99	497
3	Iodobenzene	Bu	0.2	$NaHCO_3$	8	**3a**	80	403
4	Iodobenzene	Bu	0.2	K_2CO_3	8	**3a**	>99	499
5	Bromobenzene	Bu	0.2	K_2CO_3	8	**3a**	99	498
6	Iodobenzene	Bu	0.0001	K_2CO_3	24	**3a**	94	9.38×10^{5}
7	Bromobenzene	Bu	0.0001	K_2CO_3	24	**3a**	27	2.70×10^{5}
8	2-Iodotoluene	Bu	0.0001	K_2CO_3	24	**3b**	85	8.49×10^{5}
9	3-Iodotoluene	Bu	0.0001	K_2CO_3	24	**3c**	98	9.84×10^{5}
10	4- Iodotoluene	Bu	0.0001	K_2CO_3	24	**3d**	65	6.52×10^{5}
11	4-Iodoanisole	Bu	0.0001	K_2CO_3	24	**3e**	85	8.59×10^{5}
12	4-Iodoacetophenone	Bu	0.0001	K_2CO_3	24	**3f**	71	7.11×10^{5}
13	4-Iodo-trifluorobenzene	Bu	0.0001	K_2CO_3	24	**3g**	8	8.1×10^{4}
14	1-Iodonaphthalene	Bu	0.0001	K_2CO_3	24	**3h**	96	9.63×10^{5}
15	3-Iodotoluene	Bu	0.00001	K_2CO_3	24	**3c**	65	6.53×10^{6}
16	3-Iodotoluene	Me	0.00001	K_2CO_3	24	**3i**	88	8.84×10^{6}
17	3-Iodotoluene	Me	0.0000001	K_2CO_3	24	**3i**	13	1.32×10^{8}

[a] All reactions were carried out under air.
[b] Isolated yield.

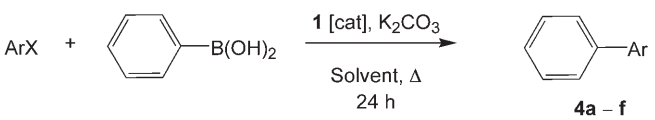
when bromobenzene was applied (Table 1, entry 7) quantifying the difference in reactivity between aryl iodides and bromides hidden in the preceeding series with a catalyst loading of 0.2 mol%. The yield strongly depends on mesomeric effects in the aryl iodides: The coupling of *ortho*-, *meta*- and *para*-iodotoluenes in the presence of 1 ppm of pincer palladium complex **1** gave **3b**, **3c** and **3d** in isolated yields of 85, 98 and 65%, respectively (Table 1, entries 8–10) corresponding to a turnover number (TON) of 9.84×10^5 for the *meta*-isomer. Good TONs were also observed for the coupling of butyl acrylate with *para*-iodoanisole (8.59×10^5) and *para*-iodoacetophenone (7.11×10^5) (Table 1, entries 11 and 12). Acceptor substituents in the aryl halide reduced the yield dramatically as demonstrated for the CF_3 derivative (Table 1, entry 13, 8%). No significant steric effect was observed as shown for 1-iodonaphthalene which afforded a 96% yield (9.63×10^5 TON) (Table 1, entry 14).

The efficiency of the catalyst was demonstrated in the coupling of *meta*-iodotoluene with butyl or methyl acrylate using a steadily reduced catalyst loading. A catalyst loading of 0.1 ppm of palladium pincer carbene complex **1** applied to butyl acrylate under standard conditions (Table 1, entry 15) gave a 65% yield (TON: 6.53×10^6) while methyl acrylate afforded an 88% isolated yield (TON: 8.84×10^6, Table 1, entry 16). The more reactive methyl acrylate even tolerated 1 ppb as a minimum loading of **1** to result in a still 13% isolated yield of **3i** (TON: 1.32×10^8; TOF: 5.50×10^6 h or 1.53×10^3/sec, Table 1, entry 17).

The Heck reaction of 4-bromoanisole and styrene (K_2CO_3, refluxing dimethylacetamide (DMA), 13 h) applying a 2 ppm catalyst loading of complex **1** resulted in 67% yield of arylated styrenes (TON: 3.36×10^5). A comparison with the highest TON (7.5×10^4) obtained with the pyridine-bridged[4c] and lutidine-bridged[4g] imidazolylidene palladium analogues applied for the same reaction (even with 20 mol% *n*-Bu_4NBr as an additive) characterizes the pyridine-bridged CNC pincer bis-benzimidazolylidene complex **1** as distinctly more efficient, reflecting its better σ-donor properties (electronic effect). In addition, steric factors may also account for the catalytic properties of complex **1** as the planar extended metal-ligand hybrid π-system ring present in complex **1** may enhance the catalytic activity owing to reduced bond angles in the twisted conformation at the metal center in comparison with its lutidine-bridged (benz)imidazolylidene analogues.[3c,4g]

Under the same conditions palladium pincer complex **1** also efficiently catalyzes the Suzuki coupling as demonstrated for aryl halides and phenylboronic acid; a catalyst loading of 1 ppm resulted in 62–97% isolated yields for the phenylation of iodobenzene and a series of *para*-halobenzenes (Table 2). As observed for the phenylation of 4-bromoacetophenone a comparison of pincer complex **1** and its imidazolylidene analogue which gave a 88% yield with 1 mol% catalyst loading and a 70% yield with 0.2 mol% catalyst loading in DMA in 30 h[4c] underlined that the catalytic activity is enhanced by the planar extention of the π-system. At 80 °C with 1 ppm catalyst loading, a 62% yield of **4d** was obtained (Table 2, entry 4), whereas an elevated temperature of 110 °C[4c] and a replacement of DMA for NMP as a solvent increased the yield to 78% (Table 2, entry 5). Even at a low loading the pincer complex catalyst **1** tolerates a variety of

Table 2. Suzuki coupling of aryl halides and phenylboronic acid catalyzed by CNC pincer palladium complex **1**.[a]



Entry	ArX	Catalyst [mol%]	Solvent	Temperature [°C]	Product	Yield [%][b]	TON
1	Iodobenzene	0.0001	NMP	140	**4a**	90	9.05×10^5
2	4-Iodotoluene	0.0001	NMP	140	**4b**	72	7.18×10^5
3	4-Iodoanisole	0.0001	NMP	140	**4c**	97	9.69×10^5
4	4-Bromoacetophenone	0.0001	NMP	80	**4d**	62[c]	6.23×10^5
5	4-Bromoacetophenone	0.0001	DMA	110	**4d**	78	7.84×10^5
6	4-Bromoacetophenone	0.0001	NMP	140	**4d**	84	8.43×10^5
7	4-Iodoacetophenone	0.0001	NMP	140	**4d**	83[d]	8.32×10^5
8	4-Iodo-trifluorobenzene	0.0001	NMP	140	**4e**	90	9.03×10^5
9	1-Iodonaphthalene	0.0001	NMP	140	**4f**	80	7.99×10^5
10	4-Iodoanisole	0.0000001	NMP	140	**4c**	25	2.48×10^8
11	4-Iodo-trifluorobenzene	0.0000001	NMP	140	**4e**	15	1.49×10^8

[a] All reactions were carried out under air.

[b] Isolated yield.

[c] In order to compare with literature data (reaction time: 30 h).

[d] Full conversion resulted in formation of a homo-coupling by-product (12% isolated yield).

substituents differing in their electronic and steric properties and allows for good yields of biphenyl derivatives **4a–e** (Table 2, entries 2–9). Nearly identical yields of **4d** have been obtained under the same conditions from 4-bromoacetophenone and 4-iodoacetophenone which, however, also gave 12% of homocoupling product after full conversion (Table 2, entries 6 and 7). The coupling of 1-iodonaphthalene is similarly effective (Table 2, entry 9, 80%) indicating that steric bulk does not hamper severely the cross-coupling even with a low catalyst loading of 1 ppm. Unlike what is observed in the Heck reactions, the Suzuki protocol tolerates a strong electron-withdrawing substituent such as in 4-iodotrifluorobenzene (Table 2, entry 8, 90%). A further decrease of the catalyst loading to 1 ppb still resulted in a 25% yield (Table 2, entry 10; TON: 2.48×10^8; TOF: 1.03×10^7 h or 2.87×10^3/sec) for coupling with 4-iodoanisole and a 15% isolated yield (Table 2, entry 11; TON: 1.49×10^8; TOF: 6.21×10^6 h or 1.72×10^3/sec) for reaction with 4-iodotrifluorobenzene.

In conclusion, the pyridine-bridged bis-benzimidazolylidene CNC pincer palladium complex **1** which is readily accessible from cheap, commercial precursors is an efficient catalyst for Heck and Suzuki cross-coupling reactions even with catalyst loadings as low as 0.1 to 1 ppm. It is stable against air, moisture and heat, and tolerates a variety of functional groups in the arene varying in their electronic and steric properties which suggests that the catalytic activity of this type of pincer complexes is significantly enhanced by the planar extended metal ligand hybrid π-system.

Experimental Section

General Remarks

All commercial reagents and solvents were used directly without further purification. All reactions were carried on air unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 DRX/400 DPX/300 DPX. ESI-mass spectra were recorded on a micrOTOF-Q from Bruker Daltonik. GC-MS: HP 5890 Series II. CEM Discover microwave instrument was applied for the palladation.

Synthesis of Pyidine-Bridged Bis-benzimidazolium Dibromide 2

A mixture of 2,6-difluoropyridine (2.99 g, 26 mmol) and benzimidazole (15.34 g, 130 mmol) was heated to 185 °C under stirring in a sealed tube for 2 h and then at 160 °C for a further 30 h. The mixture was cooled, and water was added. The precipitate was washed by hot EtOAc. The residue was dissolved in $CHCl_3$ and then reprecipitated upon addition of Et_2O to give 2,6-bis(imidazol-1-yl)pyridine as a white powder; yield: 7.6 g (94%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): $\delta=8.70$ (s, 2H), 8.10–8.17 (m, 3H), 7.89–7.95 (m, 2H), 7.60 (d, $J=8$ Hz, 2H), 7.38–7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): $\delta=149.52$, 144.64, 142.08, 141.14, 131.93, 124.82, 123.93, 120.94, 112.99, 111.36; HR-MS (MALDI): $m/z=310.1096$, calcd. for $[M-1]^+$: 310.1171.

A mixture of 2,6-bis(benzimidazol-1-yl)pyridine (0.622 g, 2 mmol) and *n*-BuBr (0.43 mL, 4 mmol) in benzonitrile (5 mL) was stirred at 160 °C for 30 h in a sealed tube. After cooling, the mixture was dissolved in $CHCl_3$ (50 mL), and then Et_2O (250 mL) was added. The crude product was purified by reprecipitation from $CHCl_3/Et_2O$ to give a white NMR-pure solid in almost quantitative yield. ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K): $\delta=9.98$ (s, 2H), 7.90 (t, $J=8$ Hz, 1H), 7.60 (d, $J=8.1$ Hz, 2H), 7.51 (d, $J=8.1$ Hz, 2H), 7.43 (d, $J=8$ Hz, 2H), 6.92–6.99 (m, 2H), 6.85–6.91 (m, 2H), 3.83 (t, $J=7.3$ Hz, 4H), 1.14–1.23 (m, 4H), 0.61 (tq, $J=7.5$ and 7.5 Hz, 4H), 0.12 (t, $J=7.3$ Hz, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz): $\delta=146.8$, 144.9, 143.3, 132.1, 130.0, 128.3, 127.8, 118.4, 116.2, 114.7, 47.7, 30.9, 19.6, 13.9; MS (ESI): $m/z=504.2$ $[M-Br]^+$, 456.3, 424.3 $[M-2Br]^+$, 368.2 $[M-2Br-Bu]^+$, 312.1 $[M-2Br-2Bu]^+$, 212.6, 184.6, 156.6; HR-MS (ESI): $m/z=504.1757$, calcd. for $[M-Br]^+$: 504.1757; anal. calcd. for $C_{27}H_{31}Br_2N_5\cdot0.5H_2O$: C 54.56, H 5.34, N 11.78; found: C 54.66, H 5.35, N 11.62.

Synthesis of Pyridine-Bridged Bis(benzimidazol-2-ylidene)palladium Complex 1

A suspension of pyridine-bridged bis-benzimidazolium dibromide **2** (0.585 g, 1 mmol) and $Pd(OAc)_2$ (0.224 g, 1 mmol) was stirred in DMSO (8 mL) for 1 h at room temperature under vacuum. After refilling the argon, the mixture was heated under stirring in the open vessel model at 160 °C for 25 min (at 40 W with a CEM Discover microwave instrument). DMSO was removed under vacuum with heating. After cooling to room temperature, the resulting residue was dissolved in 10 mL of $CHCl_3$; then Et_2O was added (100 mL) and the precipitate was collected by filtration and dried under vacuum. Another two re-precipitation operations afforded a yellowish solid; yield: 528 mg (75%). ^{1}H NMR (DMSO-d_6, 500 MHz, 298 K): $\delta=7.64$ (t, $J=8.3$ Hz, 1H), 7.55 (d, $J=7$ Hz, 2H), 7.52 (d, $J=8.3$ Hz, 2H), 7.14 (dd, $J=7$ and 2.2 Hz, 2H), 6.75–6.82 (m, 4H), 3.96 (t, $J=7.5$ Hz, 4H), 0.94 (q, $J=7.5$ Hz, 4H), 0.56 (tq, $J=7.5$ and 7.5 Hz, 4H), 0.05 (t, $J=7.5$ Hz, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz, 298 K): $\delta=175.45$, 151.43, 147.46, 134.24, 130.13, 127.78, 127.12, 114.45, 114.05, 110.61, 48.13, 32.79, 20.08, 14.54; MS (ESI): $m/z=690.0$ $[M+2]^+$, 610.1 $[M-Br+2]^+$, 564.1, 484.4, 454.3, 368.2 $[M-2Br-Bu-Pd]^+$, 298.2, 268.1, 212.6; HR-MS (ESI): $m/z=608.0640$, calcd. for $[M-Br]^+$: 608.0641; anal. calcd. for $C_{27}H_{29}Br_2N_5Pd\cdot H_2O$: C 45.82, H 4.41, N 9.89; found: C 45.44, H 4.32, N .9.55.

General Procedure for the Heck Reactions

To a suspension of K_2CO_3 (1.68 g, 12 mmol) in 10 mL NMP aryl halide (10 mmol), alkyl acrylate (11 mmol) and the CNC pincer palladium carbene complex **1** (solution in NMP) were added. The reaction mixture was heated at 140 °C (monitored by GC-MS) and then allowed to cool to room temperature. Then the reaction mixture was diluted with water, and the product was extracted with ether (3 × 20 mL). The combined extracts were dried over $MgSO_4$, the organic phase was concentrated under vacuum and the crude product was purified by flash column chromatography (hexane/EtOAc = 100/1).

General Procedure for the Suzuki Reactions

A mixture of catalyst, K_2CO_3 (1.68 g, 12 mmol), aryl halide (10 mmol) and phenyl boronic acid (1.29 g, 11 mmol) in 10 mL NMP was heated at 140 °C for 24 h. The work-up of the reaction was performed as described above for the Heck reaction.

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