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PAPER

Synthesis and characterization of *para*-pyridine linked NHC palladium complexes and their studies for the Heck–Mizoroki coupling reaction†

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This paper describes the synthesis of 1-(pyridine-4-ylmethyl) NHC and their Pd(II) and Ag(I) complexes, which are fully characterized. Interestingly, we have also synthesized a Pd complex **3a-CO$_3$** using a more direct treatment of K_2CO_3 with $PdCl_2$. **3a-CO$_3$** represents the first reported solid structure of a Pd η^2-carbonato complex stabilized by an NHC framework. **3a-CO$_3$** can be easily converted to a $PdCl_2$ derivative by treating it with chloroform. We have found these palladium complexes mediate the Heck–Mizoroki coupling with a low catalyst loading. Furthermore, we also expand such catalytic manifold toward constructing fused polyaromatic substrates, a highly useful class of compounds in optoelectronic chemistry.

Introduction

N-Heterocyclic carbenes (NHCs) are now ubiquitous in organometallic chemistry due to their effective role as ligands in homogeneous transition metal catalysis. In the last decade, most research efforts have been devoted to the development of hybrid NHC ligand sets based on covalently attaching the *ortho*-pyridyl pendant arm.[1] The interest in these scaffolds is fuelled by the chelating effect invoked by the N-donor site to enhance the stability of the resulting catalyst.[1c,2] Amazingly, no such structural NHC framework bearing a *para*-pyridyl pendant arm has been reported in the literature, despite of many reports pertaining to studies of C–C cross coupling reactions using *ortho*-pyridine NHCs as supporting chelating ligands for metal complexes.[3]

Today, palladium-catalyzed cross coupling reactions are among the most common and effective strategies employed by chemists for constructing C–C bonds in molecular synthesis,[4] which has been recognized with the Nobel Prize for Chemistry in 2010. Heck–Mizoroki coupling represents one example of a palladium-catalyzed reaction that permits a bond attachment of alkenyl substituents onto an aromatic molecule in a gentle manner. Since the pioneering work contributed by Heck and Mizoroki in the early 1970s,[5] a significant advance in this area has been achieved and applications have been found in the synthesis of natural products, pharmaceuticals, and materials science.[6] Herein, we describe the development of the 1-(pyridine-4-ylmethyl) NHC scaffold and the synthesis of their silver and palladium complexes. These palladium complexes were further tested and examined for their catalytic activity towards the Heck–Mizoroki cross coupling reaction.

Results and discussion

Synthesis of 1-(4-pyridinylmethyl) imidazolium

The preliminary work was initiated with the synthesis of 1-(pyridine-4-ylmethyl) imidazolium bearing a mesityl (**1a**) and isopropyl (**1b**) side arm. The imidazolium compounds **1a** and **1b** were prepared with a similar method to that described by Tolman *et al.*, as illustrated in Scheme 1.[7] The quaternization of **1a** and **1b** was achieved through refluxing the suspension of 4-(chloromethyl)pyridine hydrochloride with $NaHCO_3$ and mesityl–imidazole in ethanol for a day. The identity of **1** is confirmed by ^{1}H NMR spectroscopy with the signature peak of an N–CH–N fragment at ~10–11 ppm. Numerous attempts to obtain free carbene species *via* base deprotonation of compound **1** were unsuccessful and yielded intractable products.

Synthesis and characterization of pyridine linked NHC silver and palladium complexes

Considering that we are not able to obtain the free carbene species *via* deprotonation of imidazolium **1**, one alternate synthetic method for obtaining NHC complexes is through

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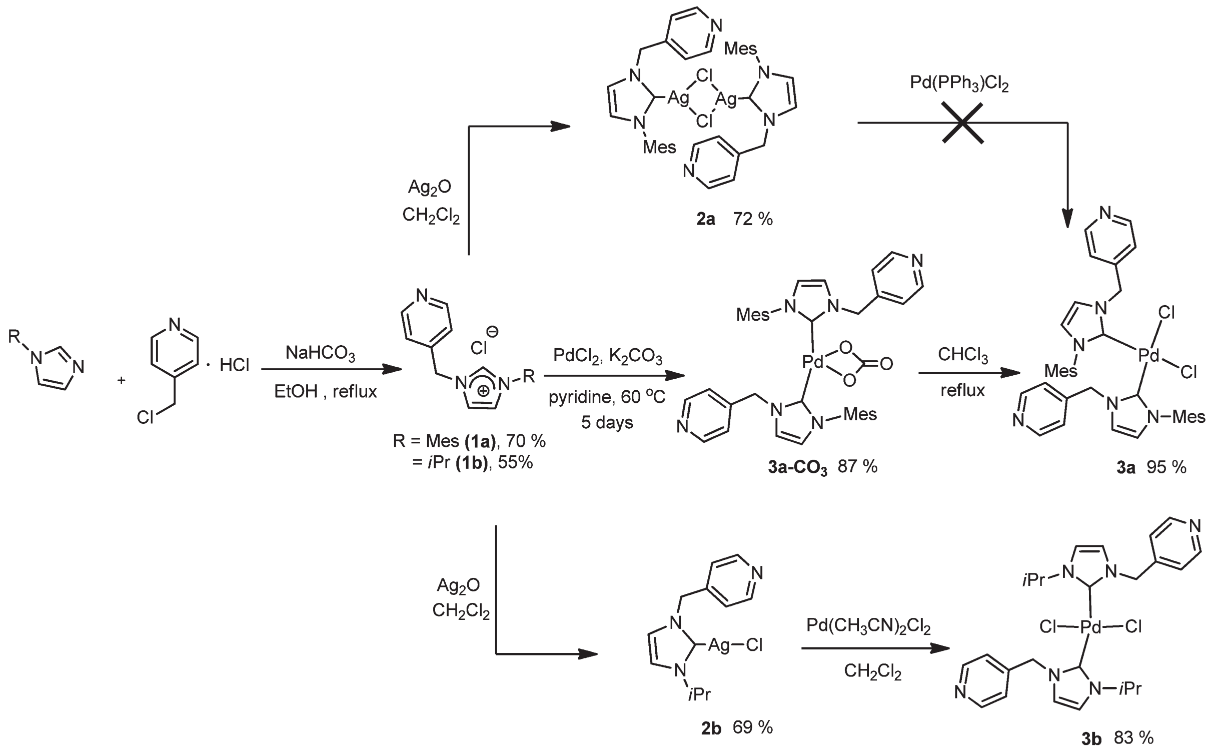
† Electronic supplementary information (ESI) available: X-ray data collection, solution, and refinement details for compounds **2a**, **2b**, **2b**, **3a**, **3b** and **3a-CO$_3$**. Crystal data are also available as CIF files for these compounds. CCDC reference numbers: 818961 (**2a**), 818962 (**2b**), 818963 (**3a**), 818964 (**3a-CO$_3$**) and 818965 (**3b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30520h



Scheme 1 Preparation of the imidazolium compounds **1a** and **1b**, Ag and Pd complexes.

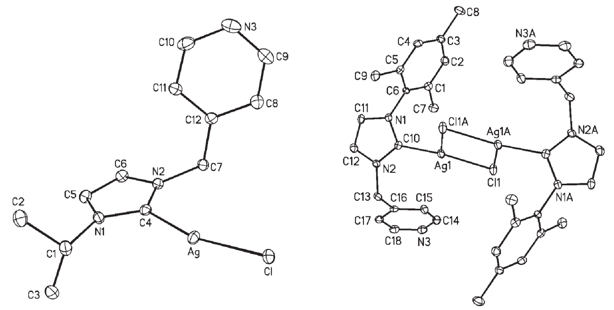


Fig. 1 Molecular structures of **2b** (left) and **2a** (right) with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

transmetallation using silver NHC complexes, which are well known for acting as carbene transfer agents.[8] The reaction of **1** and Ag_2O in dichloromethane at room temperature produces compound **2** in a reasonable yield (**2a** (72%) and **2b** (69%)). A single-crystal X-ray diffraction experiment was undertaken to determine the atomic connectivity in **2a** and **2b**, and structural models are presented in Fig. 1, which are consistent with the NMR spectroscopy and molecular mass analysis. The structure of **2b** consists of a linear arrangement of Ag coordinated to NHC and chloride ligands with the Ag–C(4) distance being 2.081(2) Å, which is in agreement with the observed average for five-membered carbene complexes.[9]

In contrast to **2b**, the molecular structure of **2a** consists of two independent silver NHC dimer units bridged by chloride ligands. Each unit seems to have an inversion point positioned at the center of Ag–Cl–Ag bridging. The buried volume, a gauge for the measurement of steric constraints, indicated that mesityl is obviously larger than isopropyl.[10] This is counter-intuitive to the anticipated structural behavior, where a metallic complex bearing a ligand with a large steric protection should appear to disfavor this dimerization or aggregation process like **2b**. Yet, the mesityl N substituent of **2b** can rotate more freely than the isopropyl group of **2a**, permitting fluctuations in the steric interactions.[11] Interestingly, the bond distance of Ag–carbene in **2a** (Ag–C(10) 2.078(4) Å) has not been perturbed significantly by the change of the pendant arm with respect to **2b**. Finally, the crystal packing in **2a** and **2b** demonstrated a lack of intermolecular interaction between Ag and the pyridyl moiety, signifying that the strong σ donation from the NHC has a saturated metal center from accepting a higher electron density from the other ligand.

We then turned to the synthesis of Pd complexes by examining the transmetallation method through the corresponding Ag–NHC complexes. Ag complex **2b**, an isopropyl side arm analogue, reacts readily with $Pd(CH_3CN)_2Cl_2$ to produce a yellow solid **3b** with a high yield. The representative ^1H NMR spectroscopic features of **3b** display two singlets corresponding to a total of 4 protons at 5.76 and 5.48 ppm for methylene moieties and two doublets at 1.61 and 1.38 ppm corresponding to a total of 12 protons for the methyl group for the isopropyl arms. Nonetheless, the NMR spectra of **3b** gave little in the way of confirmation of the structure,[12] as only minimal differences in chemical shifts were observed relative to the Ag complex **2b**. A crystal of **3b** suitable for single-crystal X-ray structural analysis was obtained from a concentrated dichloromethane solution and crystallized in the triclinic $P\bar{1}$. The molecular structure of **3b** is illustrated in Fig. 2, and the crystal data and collection parameters are given in Table S5 (see the ESI†). The Pd center has a square planar geometry with the two *trans* NHC ligands, whose

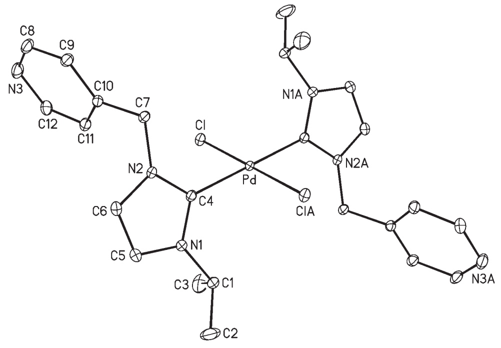


Fig. 2 Molecular structure of **3b** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

nonbonded pyridyl wing tips are *anti* to each other. The NHC rings are orthogonal to the coordination plane of the metal center with a twist angle of 69.1°, presumably minimizing the unfavourable steric interaction. The bond length between Pd and $C_{carbene}$ in **3b** is 2.0265(19) Å, which is in agreement with the typical literature value.[13]

Regrettably, an NHC Pd complex similar to **3a** cannot be prepared *via* a silver transmetallation route in a clean fashion. Therefore, we resorted to preparing the palladium complex based on a similar method to that described by Lee *et al.*[14] A direct reaction between imidazolium precursors **1a**, $PdCl_2$, and K_2CO_3 in pyridine produces **3a-CO₃** with a high yield (87%). The proton NMR spectrum of **3a-CO₃** has similar features to its silver counterpart. In addition to the carbenic peak at 167 ppm, the ^{13}C NMR spectrum of **3a-CO₃** appears to have a low field resonance at 170 ppm, indicating the possibility of a carbonate moiety in the complex. The identity of **3a-CO₃** was unambiguously confirmed by X-ray crystallography (Fig. 3), crystallizing in the monoclinic *P*2(1)/*n* and displaying a non-ideal square planar palladium(II) bound to two pyridine–NHCs in *cis* fashion with a normal length of 1.973 and 1.980 Å and one η^2-coordinated carbonate ligand with a Pd–O bond length of 2.051 and 2.041 Å. The geometrical distortion in **3a-CO₃** with a bite angle of C10–Pd–O2 99.77(8)° and C28–Pd–O1 103.19(8)° is due to the constraint of the four-membered metallacycle imposed by the carbonate coordination. Few molecular structures of the related carbonate palladium complexes supported by chelating amine and phosphine ligands have been isolated and reported.[15] To the best of our knowledge, **3a-CO₃** represents the first reported solid structure Pd η^2-carbonate complex stabilized by an NHC framework. More importantly, we are able to synthesize a high yield of **3a-CO₃** using a more direct treatment of K_2CO_3 with $PdCl_2$, rather than through CO_2 gas bubbling.

Finally, the synthesis of the pyridine–NHC palladium chloride complex **3a** is straightforward *via* **3a-CO₃**. Refluxing **3a-CO₃** in $CDCl_3$ solution produced **3a** with a quantitative yield. Like **3b**, **3a** exhibits a square planar geometry, warranting no further comment (Fig. 4) with the exception that both chloride ligands are *cis* to each other.

Catalytic Heck–Mizoroki coupling

The catalytic performance of complex **3** in the Heck–Mizoroki coupling of aryl halides with alkenes was evaluated. Initial screening attempts were undertaken to determine the viability of various bases with a 5 mol% loading of **3b** pre-catalysts for the C–C coupling of styrene (**10**) and bromobenzene (**20**) in a DMF solution at 130 °C (entries 1–3, Table 1). As seen in entry 1 of Table 1, the reaction produced a quantitative yield of the corresponding product, stilbene (**20aa**) in the presence of K_2CO_3, a milder base. However, lowering the reaction temperatures to 100

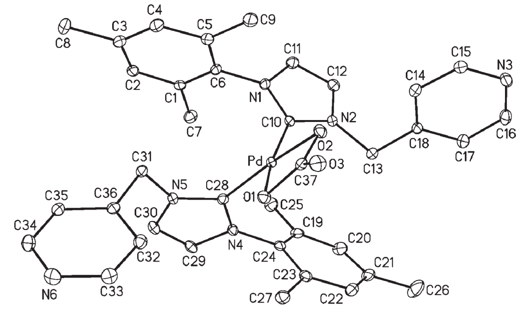


Fig. 3 Molecular structure of **3a-CO₃** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

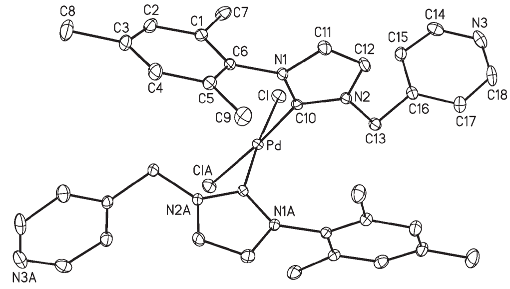
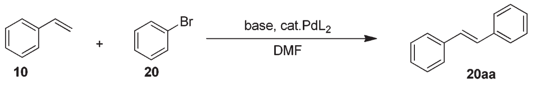


Fig. 4 Molecular structures of **3a** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.

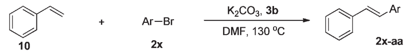
Table 1 Optimization of Heck–Mizoroki coupling in different conditions[a]

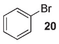
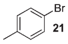
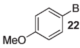
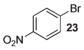
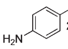
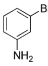
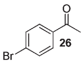
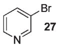
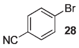
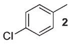


Entry	Cat./mol%	Base	Solvent	Temp (°C)	Time (h)	Yield[b]
1	**3b**/5	K_2CO_3	DMF	130	18	>95%
2	**3b**/5	KO*t*Bu	DMF	130	18	5%
3	**3b**/5	NaO*t*Bu	DMF	130	18	16%
4	**3b**/5	K_2CO_3	DMF	100	18	80%
5	**3b**/5	K_2CO_3	DMF	60	18	6%
6	**3b**/1	K_2CO_3	DMF	130	18	>95%
7	**3b**/1	K_2CO_3	DMF	130	12	>95%
8	**3b**/1	K_2CO_3	DMF	130	6	83%
9	**3b**/0.1	K_2CO_3	DMF	130	18	>95%
10	**3b**/0.1	K_2CO_3	DMF	130	12	79%
11	**3a**/0.1	K_2CO_3	DMF	130	18	92%
12	**3a-Co₃**/0.1	K_2CO_3	DMF	130	18	83%

[a] The reactions were carried out using **10** (1.92 mmol) and **20** (1.28 mmol). [b] The isolated yield is based on **20** as the limiting reagent.

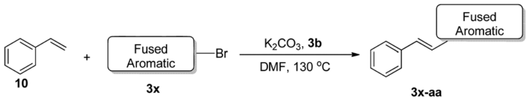
Table 2 Scope of the Heck–Mizoroki catalytic reaction with different aryl bromides[a]

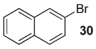
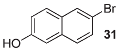
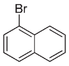
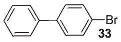
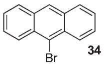
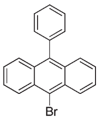
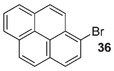
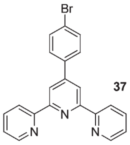


Entry	Ar–Br	Cat. PdL$_2$	Time (h)	Yield[b]
1	 20	0.1%	18	>95%
2	 21	0.1%	18	>95%
3	 22	0.1%	18	>95%
4	 23	0.1%	18	>95%
5	 24	1% 0.1%	12 18	46% 45%
6	 25	1% 0.1%	12 18	>95% 70%
7	 26	1% 0.1%	12 18	82% 69%
8	 27	1% 0.1%	12 18	67% 12%
9	 28	0.1%	18	88%
10	 29	0.1%	18	0%

[a] The reactions were carried out using **10** (1.92 mmol) and **2x** (1.28 mmol). [b] The isolated yield is based on aryl halide as the limiting reagent.

Table 3 Scope of the Heck–Mizoroki catalytic reaction with fused polyaromatic bromide[a]



Entry	Ar–Br	Cat. PdL$_2$	Time (h)	Yield[b]
1	 30	0.1%	18	86%
2	 31	0.1%	18	41%
3	 32	0.1%	18	>95%
4	 33	0.1%	18	82%
5	 34	0.1%	18	80%
6	 35	0.1%	18	81%
7	 36	0.1%	18	81%
8	 37	0.1%	18	90%

[a] The reactions were carried out using **10** (1.92 mmol) and **3x** (1.28 mmol). [b] The isolated yield is based on aryl halide as the limiting reagent.

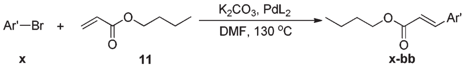
and 60 °C caused the reaction to proceed slowly with 80% and 6% yields, respectively (entries 4 and 5, Table 1). Importantly, the reactions could be performed using only 1.0 and 0.1 mol% catalyst loading with little effect on the yield (entries 6 and 9, Table 1). Next, screening of a similar catalytic reaction with the other Pd complexes **3a** and **3a-CO$_3$** also underwent an effective cross coupling of ~90% yield (entries 11 and 12, Table 1).

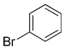
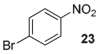
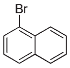
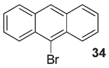
With these results in hand, we further expanded the scope of the cross coupling of styrene with different substituted aryl bromides using catalyst **3b** (see Table 2). In general, cross coupled products can be obtained with high yield, and are insensitive to the effect of electron donating or withdrawing substituted on aryl bromide (entries 1–4, 7 and 9, Table 2). A moderate conversion (67%) could also be achieved for the pyridine functionality compound (entry 8, Table 2). Electron-rich substrates with *para*-amino substituents produced a lower yield of 45% product **24aa** under identical conditions (entry 5, Table 2), but surprisingly, *meta*-amino substituents delivered a quantitative conversion (entry 6, Table 2). Regrettably, aryl chloride could not be converted effectively (entry 10, Table 2).

Fused polyaromatic compounds have been widely employed in many optoelectronic applications such as light-emitting materials,[16] organic thin-film transistors,[17] nonlinear two-photon absorption,[18] photovoltaics,[19] and bio-imaging materials.[20] In order to demonstrate the broader applicability of the method we further set out to examine the coupling of styrene with fused polyaromatic substrates in a similar reaction condition, as listed in Table 3. Excellent conversion was observed for 2-bromonaphthalene (86%, entry 1, Table 3), 1-bromonaphthalene (>95%, entry 13, Table 3) and 4-bromobiphenyl (82%, entry 4, Table 3), yet diminishing yield was seen for 6-bromo-2-naphthalenol (41%, entry 2, Table 3), suggesting the sensitivity of the reaction to a hydroxy functional group. A fused aromatic containing more than four membered rings, such as 9-bromoanthracene **34** (entry 5, Table 3), 9-bromo-10-phenylanthracene **35** (entry 6, Table 3) and pyrene **36** (entry 7, Table 3), also participated in the catalytic reaction in surprisingly high yields with low catalyst loading.

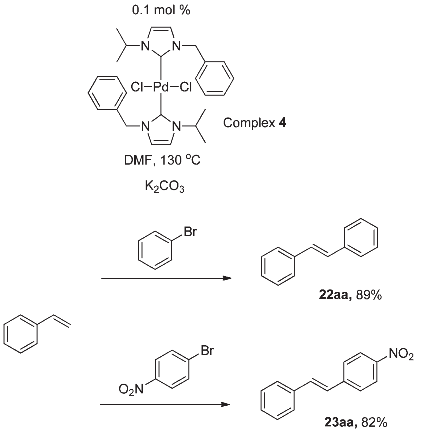
We next examined whether **3b** could also facilitate the reaction with terpyridine, as such molecular motifs have now evoked widespread attention in the area of supramolecular and coordination chemistry for materials with unique physical properties.[21] The tridentate functionality of this substrate might partially poison the catalysts. To our delight, product derived from **37** was isolated with a 90% yield (entry 8, Table 3). Moreover, the presence of dangling pyridyl groups in catalyst **3b** did not produce any notable steric hindrance for large substrates approaching the catalyst (entries 6–8, Table 3). Finally, Table 4 reveals that we can also expand the scope of our catalytic reaction to butyl acrylate with different aryl bromides as well as fused aromatic rings in high yields.

Table 4 Scope of Heck–Mizoroki catalytic reaction with butyl acrylate[a]



Entry	Ar–Br	Cat. PdL_2	Time (h)	Yield[b]
1	 **20**	0.1%	18	>95%
2	 **23**	0.1%	18	>95%
3	 **32**	0.1%	18	>95%
4	 **34**	0.1%	18	68%

[a] The reactions were carried out using **11** (1.92 mmol) and aryl bromide (1.28 mmol). [b] The isolated yield is based on aryl halide as the limiting reagent.



Scheme 2 Heck–Mizoroki coupling reaction mediated by complex **4**.

Several observations with these Pd(II) NHC catalysts employed in the Mirozoki–Heck coupling reactions are worth mentioning. Control experiments using complex **4**,[22] lacking a pyridine moiety at the *para* position, led to lower yield of 89% and 82% for **22aa** and **23aa**, respectively (Scheme 2). Second, we also performed another catalytic reaction under similar conditions with 0.3 mol% and 10 mol% of lithium chloride as an additive to bind the pedant arm of the pyridine. Again, diminishing yields of the product with 30% and 0%, respectively, were obtained. All these findings have validated the importance of the cooperative effect invoked by the pyridine moiety to assist the efficiency of this catalytic process.

Conclusions

In conclusion, this paper describes the synthesis of 1-(pyridine-4-ylmethyl) NHC and their Pd(II) and Ag(I) complexes, which are fully characterized including X-ray crystal structures. We are also able to synthesize the Pd complex **3a-CO_3** with a high yield using a more direct treatment of K_2CO_3 with $PdCl_2$. **3a-CO_3** can be easily converted to a $PdCl_2$ derivative by treating it with chloroform. We have found that the palladium catalyst **3b** actively mediates Mirozoki–Heck coupling with a low catalyst loading and a broad substrate scope. In particular, catalyst **3b** can be applied to substrates with electron donating groups (Table 2, entries 3 and 6) and a catalyst poison site (Table 2, entry 8 and Table 3, entry 8). Even a challenging substrate like naphthol gave an encouraging yield (Table 3, entry 2). We can also expand such a catalytic manifold toward other fused polyaromatic substrates. Ongoing work is focused on understanding such cooperative effects exhibited by an uncoordinated pyridine moiety and exploring the scope of other new organic reactions.

Experimental

General procedure

All air-sensitive manipulations were performed under an atmosphere of nitrogen using the Schlenk technique and/or a glovebox. Toluene, hexane, THF and ether were purified by passage through a column of activated alumina using a solvent purification system purchased from Innovative Technology, Inc. Deuterated benzene and toluene were dried by vacuum transfer from activated molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 MHz, Bruker 400 MHz and Bruker 500 MHz spectrometers using the residual proton signal in the deuterated solvent as a reference. $PdCl_2$ was purchased from Arcos Chemicals and used without further purification.

N-Mesityl-*N′*-(4-pyridylmethyl)imidazolium chloride (1a)

The compound **1a** was prepared in a similar manner to that reported by Tolman *et al.*[7] Mesityl imidazole (21.95 mmol, 4.08 g) was added to the suspension of 4-(chloromethyl)pyridine hydrochloride (18.24 mmol, 3.00 g) and sodium bicarbonate (27.36 mmol, 2.10 g) in 50 mL ethanol. After being stirred and refluxed for 18 h, volatiles were removed *in vacuo* to produce the crude product. This was dissolved in dichloromethane (100 mL), and diethyl ether (400 mL) was added slowly to precipitate the solid. Yield: 55% (3.15 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 10.91 (s, 1H, NC*H*N), 8.58 (d, $^3J_{H-H}$ = 6 Hz, 2H, Py), 7.97 (s, 1H, C*H*), 7.58 (d, $^3J_{H-H}$ = 6 Hz, 2H, Py), 7.12 (s, 1H, C*H*), 6.94 (s, 2H, C_6H_2), 6.09 (s, 2H, $PyCH_2$), 2.29 (s, 3H, $ArCH_3$), 1.99 (s, 6H, $ArCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 150.8 (Py), 143.0 (Py), 141.5 (Ar), 138.7 (NCHN), 134.1 (Ar), 130.8 (Ar), 130.0 (Ar), 123.8 (CH), 123.6 (Py), 123.5 (CH), 51.6 ($PyCH_2$), 21.2 ($ArCH_3$), 17.7 ($ArCH_3$); HR-MS (FAB): *m*/*z* = 278.1658; calculated for $C_{18}H_{20}N_3$ ($[M - Cl]^+$): 278.1658.

N-(i-Propyl)-*N′*-(4-pyridylmethyl)imidazolium chloride (1b)

The compound **1b** was prepared in a similar manner to that reported by Tolman *et al.*[7] Isopropyl imidazole (29.30 mmol, 3.28 g) was added to the suspension of 4-(chloromethyl)pyridine hydrochloride (24.40 mmol, 4.00 g) and sodium bicarbonate (35.60 mmol, 3.075 g) in 50 mL ethanol. After being stirred and refluxed for 18 h, volatiles were removed *in vacuo* to produce a brown liquid residue, which was dissolved in 50 mL dichloromethane, followed by the addition of 400 mL diethyl ether to precipitate the product. Yield: 70% (4.06 g); ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 11.09 (s, 1H, NC*H*N), 8.54 (d, $^{3}J_{\text{H–H}}$ = 5.6 Hz, 2H, Py), 7.62 (s, 1H, C*H*), 7.47 (d, $^{3}J_{\text{H–H}}$ = 6 Hz, 2H, Py), 7.41 (s, 1H, C*H*), 5.76 (s, 2H, PyCH_2), 4.71 (m, 1H, C*H*), 1.56 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 150.2 (Py), 142.3 (Py), 136.0 (N*C*N), 123.1 (Py), 122.6 (*C*H), 120.4 (*C*H), 53.1 (Py*C*H_2), 51.0 (CH), 22.7 (CH_3); HR-MS (FAB): *m/z* = 202.1348; calculated for $C_{12}H_{16}N_3$ ([M − Cl]$^+$): 202.1344.

[*N*-Mesityl-*N*′-(4-pyridylmethyl)imidazol-2-ylidene] silver chloride complex (2a)

Ag_2O (0.48 mmol, 0.11 g) in 3 mL dichloromethane solution was added to a solution of *N*-mesityl-*N*′-(4-pyridylmethyl)imidazolium chloride **1a** (0.96 mmol, 0.30 g) at room temperature. After stirring for 4 h, the solution was filtered and removed *in vacuo* to produce the solid product, which was washed with diethyl ether. Yield: 72% (0.291 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.60 (d, $^{3}J_{\text{H–H}}$ = 5.2 Hz, 2H, Py), 7.14 (s, 1H, C*H*), 7.08 (d, $^{3}J_{\text{H–H}}$ = 5.2 Hz, 2H, Py), 6.99 (s, 1H, C*H*), 6.94 (s, 2H, C_6H_2), 5.44 (s, 2H, PyCH_2), 2.31 (s, 3H, ArCH_3), 1.96 (s, 6H, ArCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 182.1 (NC*H*N), 150.4 (py), 144.8 (Ar), 139.6 (Ar), 135.1 (Ar), 134.5 (py), 129.4 (Ar), 123.6 (CH), 121.9 (CH), 121.8 (py), 54.1 (pyCH_2), 21.0 (ArCH_3), 17.6 (ArCH_3); HR-MS (FAB): *m/z* = 661.2218; calculated for $C_{36}H_{38}N_6Ag$ ([M − Cl]$^+$): 661.2209; anal. calculated (%) for $C_{36}H_{38}N_6ClAg$: C 51.27, H 4.78, N 9.96; found: C 51.39. H 4.47, N 9.85.

[*N*-(i-Propyl)-*N*′-(4-pyridylmethyl)imidazol-2-ylidene] silver chloride complex (2b)

Ag_2O (0.86 mmol, 0.20 g) in 3 mL dichloromethane solution was added to a solution of *N*-isopropyl-*N*′-(4-pyridylmethyl)imidazolium chloride **1b** (1.68 mmol, 0.40 g) at room temperature. After stirring for 4 h, the solution was filtered and removed *in vacuo* to produce the solid product, which was washed with diethyl ether. Yield: 69% (0.397 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.55 (d, $^{3}J_{\text{H–H}}$ = 6 Hz, 2H, Py), 7.07 (s, 1H, C*H*), 7.05 (d, $^{3}J_{\text{H–H}}$ = 5.6 Hz, 2H, Py), 6.95 (s, 1H, C*H*), 5.28 (s, 2H, PyCH_2), 4.72 (m, 1H, C*H*), 1.45 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 179.7 (N*C*NH), 150.7 (Py), 144.7 (Py), 122.2 (Py), 121.5 (*C*H), 118.5 (*CH*), 54.7 (Py*CH*$_2$), 54.6 (*C*H), 24.0 (*C*H_3). HR-MS (FAB): *m/z* = 308.0321; calculated for $C_{12}H_{15}N_3Ag$ ([M − Cl]$^+$): 308.0317.

[*N*-Mesityl-*N*′-(4-pyridylmethyl)imidazol-2-ylidene] palladium (II) carbonate complex (3a-CO_3)

The compound **4a** was prepared in a similar manner as that described by Lee *et al.*[14] A suspension of **1a** (0.63 mmol, 0.20 g), K_2CO_3 (2.56 mmol, 0.36 g), and $PdCl_2$ (0.32 mmol, 0.06 g) in 3 mL pyridine was heated at 60 °C for 5 days. The reaction mixture was allowed to cool down and was removed *in vacuo* to produce the solid residue. The solid residue was redissolved in 15 mL dichloromethane and washed twice with water to remove the excess inorganic salt. The washed solution was dried *in vacuo* to produce a yellow solid, which was further purified by recrystallization from CH_2Cl_2–diethyl ether (3 : 1 volume) at 25 °C. Yield: 87% (0.20 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.55 (d, $^{3}J_{\text{H–H}}$ = 6 Hz, 2H, P), 7.18 (d, $^{3}J_{\text{H–H}}$ = 5.6 Hz, 2H, Py), 7.13 (s, 1H, C_6H_2), 7.06 (s, 1H, C_6H_2), 6.82 (d, 1H, C*H*), 6.77 (d, 1H, C*H*), 5.54 (d, $^{2}J_{\text{H–H}}$ = 14.8 Hz, 1H, PyCH_2), 3.83 (d, $^{2}J_{\text{H–H}}$ = 14.8 Hz, 1H, PyCH_2), 2.42 (s, 3H, ArCH_3), 2.18 (s, 3H, ArCH_3), 1.61 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 170.2 (CO_3), 167.5 (NC*H*N), 150.9 (Ar), 143.8 (Ar), 140.2 (Ar), 139.0 (Ar), 135.3 (Ar), 133.5 (Ar), 130.9 (Ar), 129.1 (Ar), 124.4 (CH), 123.7 (Ar), 121.2 (CH) 52.8 (PyCH_2), 21.3 (ArCH_3), 19.0 (ArCH_3), 17.7 (ArCH_3); ν_{max}/cm^{-1} 1618s (CO); HR-MS (EI): *m/z* = 721.2121; calculated for $C_{37}H_{39}N_6O_3Pd$ ([M + H]$^+$): 721.2118.

[*N*-Mesityl-*N*′-(4-pyridylmethyl)imidazol-2-ylidene] palladium (II) chloride complex (3a)

The 3 mL dichloromethane solution of NHC Pd complexes **4a** (0.27 mmol, 0.20 g) was stirred at 60 °C for 3 days. The cloudy solution was filtered through Celite. The filtrate solution was dried *in vacuo* to produce a pure color solid product. Yield: 95% (0.19 g). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 8.56 (d, $^{3}J_{\text{H–H}}$ = 6 Hz, 2H, Py), 7.22 (s, 1H, C_6H_2), 7.20 (d, $^{3}J_{\text{H–H}}$ = 5.6 Hz, 2H, Py), 7.15 (s, 1H, C_6H_2), 6.86 (d, 1H, C*H*), 6.31 (d, 1H, C*H*), 5.54 (d, $^{2}J_{\text{H–H}}$ = 15.2 Hz, 1H, PyCH_2), 3.64 (d, $^{2}J_{\text{H–H}}$ = 15.2 Hz, 1H, PyCH_2), 2.49 (s, 3H, ArCH_3), 2.39 (s, 3H, ArCH_3), 1.59 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C): δ 163.6 (NC*H*N), 150.3 (py), 143.9 (Ar), 140.1 (Ar), 139.5 (Ar), 135.2 (Ar), 133.9 (Ar), 131.1 (Ar), 129.0 (Ar), 124.2 (CH), 124.1 (Py), 121.2 (CH) 52.7 (Py*C*H_2), 21.2 (Ar*C*H_3), 19.9 (Ar*C*H_3), 18.1 (Ar*C*H_3).

[*N*-(i-Propyl)-*N*′-(4-pyridylmethyl)imidazol-2-ylidene] palladium (II) chloride complex (3b)

$Pd(CH_3CN)_2Cl_2$ (0.87 mmol, 0.30 g) in dichloromethane was added to the suspension of **2b** (0.44 mmol, 0.11 g) at room temperature and was stirred for 4 h. The cloudy solution was filtered through Celite. The filtrate solution was dried *in vacuo* to produce a pure solid product. Yield: 83% (0.210 g); ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.61 (br, 2H, Py), 8.46 (br, 2H, Py), 7.38 (d, $^{3}J_{\text{H–H}}$ = 5.2 Hz, 2H, Py), 7.15 (d, $^{3}J_{\text{H–H}}$ = 4.8 Hz, 2H, Py), 6.94 (d, $^{3}J_{\text{H–H}}$ = 1.6 Hz, 1H, C*H*), 6.90 (d, $^{3}J_{\text{H–H}}$ = 1.6 Hz, 1H, C*H*), 6.73 (d, $^{3}J_{\text{H–H}}$ = 1.6 Hz, 1H, C*H*), 6.69 (d, $^{3}J_{\text{H–H}}$ = 1.6 Hz, 1H, C*H*), 5.76 (s, 2H, PyCH_2), 5.68 (m, 1H, C*H*), 5.50 (s, 2H, PyCH_2), 5.35 (m, 1H, C*H*), 1.62 (d, 6H, CH_3), 1.40 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): 170.4 (NCN), 170.4 (NCN), 150.4 (Py), 150.3 (Py), 145.6 (Py), 145.4 (Py), 122.9 (Py), 122.6 (Py), 121.2 (CH), 121.10 (CH), 117.7 (CH), 53.2 (CH), 53.0 (CH), 52.5 (CH), 23.7 (CH_3), 23.5 (CH_3); HR-MS (EI): *m/z* = 579.1023; calculated for $C_{24}H_{31}N_6C_{12}Pd$ ([M + H]$^+$): 579.1022.

General procedure for the palladium-mediated Heck–Mirozoki coupling of styrene with various aryl halides

K_2CO_3 base was added to a DMF solution of **3b** (0.1 mol%) and styrene **10** or butyl acrylate **11** (1.92 mmol) and aryl halide (1.28 mmol) in a Schlenk tube, and stirred with heating at 130 °C for several hours. The resulting mixture was filtered through Celite and the filtrate solution was concentrated *in vacuo* to produce the crude product. The crude product was further purified by flash chromatography using hexane/ethyl acetate as the eluent.

Single-crystal X-ray characterization

X-ray data collection, solution, and refinement details for **2a**, **2b**, **3a** and **3b** and **3a-CO$_3$** are included in the ESI.† Crystals were mounted using viscous oil or epoxy adhesive onto glass fibers and cooled to the data collection temperature. Data were collected using a Nonius Kappa CCD diffractometer (MoK$_\alpha$ = 0.71073 Å). Multi-scan absorption corrections were employed. The structures were solved by direct methods and refined using the least-squares method on F^2. The compound molecule **2a** is located with two symmetry independent molecules, each on an inversion center. In **3a**, the molecule is located on a two-fold axis with *cis* ligands, while in **3b** the *trans* molecule is located on an inversion center. One molecule of methylene chloride solvent was found co-crystallized per compound molecule in **3a-CO$_3$**. All non-hydrogen atoms were refined with anisotropic displacement parameters. Amine hydrogen atoms were located from the difference map and refined with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached nitrogen atom. All other hydrogen atoms were treated as idealized contributions. The structure factors and anomalous dispersion coefficients are contained in the SHELXTL 6.12 program library.[23] CCDC-818961 (**2a**), CCDC-818962 (**2b**), CCDC-818963 (**3a**), CCDC-818964 (**3a-CO$_3$**) and CCDC-818965 (**3b**) contain the supplementary crystallographic data for this paper.

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