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FULL PAPER

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Palladacycles bearing COOH-/ester-functionalized N-heterocyclic carbenes: Divergent syntheses and catalytic applications

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Two new [C^N]-type palladacyclic dinuclear complexes bearing carboxylate-containing N-heterocyclic carbenes (NHCs) were synthesized, and in both cases the carboxylato-NHC ligand adopts a bridging mode. Both complexes proved to be suitable precursors, which can be used to divergently access palladacycles bearing ester- or COOH-functionalized NHCs upon esterification or acidolysis. In the esterification reactions, alkyl halides are found to selectively react with the carboxylato moieties, and the palladacycle scaffold is retained even when excess haloalkane is employed. In the acidolysis reactions, the desired COOH-tethered complexes can only be obtained when stoichiometric acid (with respect to Pd) is used, while excess acid destroys the metallacycle scaffold. Finally, a preliminary catalytic study reveals the good performances of all newly synthesized complexes in direct aromatic C—H functionalization reactions with alkynes. Poisoning experiments indicate that these hydroarylation reactions are likely to be homogeneously catalyzed.

KEYWORDS
N-heterocyclic carbene, palladacycle

1 | INTRODUCTION

Over the past decade, the chemistry of N-heterocyclic carbenes (NHCs) has experienced a rapid development.[1] In contrast to the extensively studied phosphines, one of the notable advantages of NHCs is the relative ease of ligand functionalizations.[2] The incorporation of additional donors to the arms of NHCs confers on the corresponding complexes enhanced stabilities and tunable stereoelectronic properties.[3] In addition, functionalized NHCs also render feasible the immobilization of carbene complexes onto various solid supports, which can be employed to access heterogeneous catalysts.[4] In this regard, the attachment of O-containing moieties (e.g. carboxylates, esters, ethers, etc.) to NHCs is particularly attractive, since such a combination of a hard (oxygen, typically hemilabile) and soft (carbon, typically spectating) donor atom in a single ligand can in principle assist the stabilization of metal centers, which has found manifold applications especially in metal-mediated catalysis. Recently, this research area has been comprehensively reviewed by Braunstein and co-workers.[2f]

NHC-based palladacycles of type **I** (Figure 1), combining the structural benefits of metallacycle scaffolds[5] and NHCs, can be regarded as analogues of well-established phosphine-based palladacycle precatalysts (e.g. Buchwald type,[6] Indolese–Studer type,[7] etc.) and have attracted rapidly growing interest in recent years. Such motifs reported by Nolan *et al.*[8] and others[9] have exhibited outstanding catalytic performances in various organic transformations.

Notably, despite the fact that donor-functionalized NHCs (df-NHCs) can impart potential advantages to

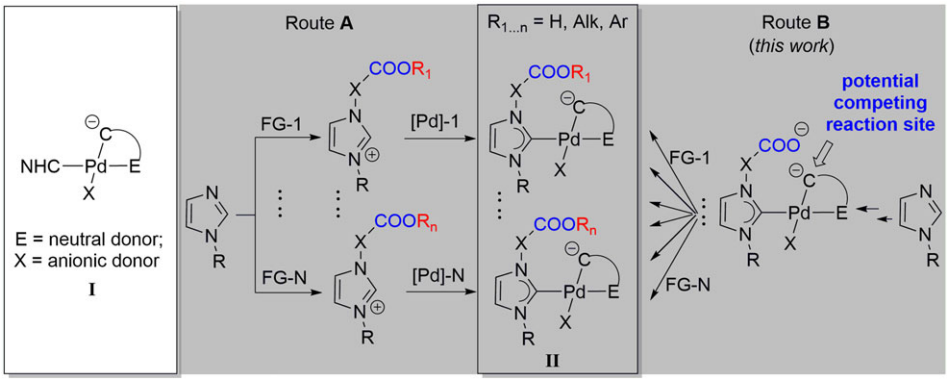


FIGURE 1 NHC-based palladacycle **I**, and comparison of pre-functionalization route A versus divergent functionalization route B to synthesize the target complexes **II**

corresponding complexes and facilitate their applications (*vide supra*), the syntheses and catalysis of palladacycles **I** bearing df-NHCs have received little attention, and only a small number of scattered examples[10] have been hitherto known. These prior works inspired us to explore the syntheses of such palladacycles bearing carboxylic acid-/ester-functionalized NHCs (**II**, Figure 1). The choice of carboxylate-based groups is not only due to the benefit brought by O-containing functionalities (*vide supra*) but also because of their rich organic chemistry easing their further potential modifications.

Based on the background discussed above and our continuing interest in carbene chemistry, herein we report the syntheses of palladacycles bearing carboxylate-anchored NHCs. Their reactivities in acidolyses/esterifications were also systematically investigated. Comparative catalytic studies including poisoning experiments were also carried out employing the newly synthesized df-NHC palladacycles as precatalysts in direct C—H functionalizations with alkynes.

2 | RESULTS AND DISCUSSION

Although the target complexes (**II**) can be accessed via a traditional 'pre-functionalization' route (route A, Figure 1),[11] a more attractive 'post-modification' route[12] (route B, Figure 1) will be explored herein, since this strategy is highly modular and divergent (route B versus route A). However, it should also be noted that the acidolyses/esterifications[13] designed in route B may undermine the metallacycle rending this route less straightforward, since palladacyclic complexes especially those bearing strongly electron-releasing carbanions are known to undergo various competing reactions (e.g. acidolyses, oxidative additions, etc.).[14]

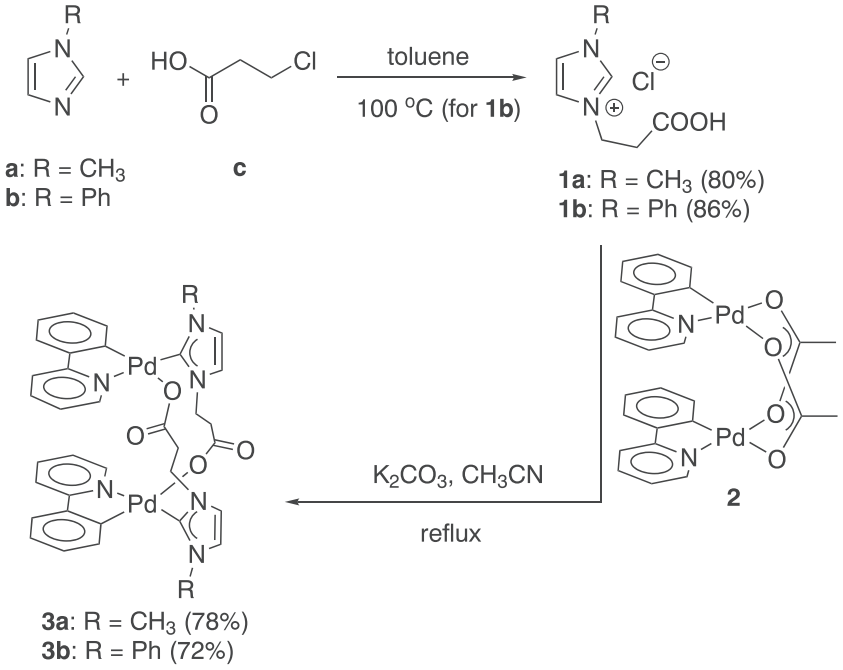
2.1 | Syntheses of carboxylate-NHC palladium precursors

Two COOH-functionalized imidazolium salts **1a** and **1b** were prepared (Scheme 1). Compound **1a** was accessed following a slightly modified procedure,[15] and salt **1b** was newly synthesized and further fully characterized. Notably, the COOH proton survives from the elimination with the chloride anion, and no formation of betaine-like species was observed.

Subsequent palladations with acetato-bridged dimeric precursor $[Pd(\mu\text{-}CH_3COO)(Ppy)]_2$ (**2**; Ppy = 2-(2-pyridinyl)phenyl-κ*C*,κ*N*) in the presence of K_2CO_3 led to the formation of two dinuclear complexes **3a** and **3b**, in which the carboxylate-tethered imidazolin-2-ylidenes serve as bridging ligands. Notably, in previous studies, carboxylate ion-anchored NHCs predominantly adopt monodentate (carbene-ligated) or chelating coordination fashions.[16] Such bridging modes have been reported for df-NHCs bearing other types of functionalities such as oxazolines and pyridines.[17]

Complexes **3a** and **3b** were isolated as pale yellow solids, which are considerably stable even in solution. In addition, **3a** and **3b** show poor solubility in common organic solvents such as dimethylsulfoxide (DMSO), CH_2Cl_2 and CH_3OH, probably due to their rigid dimeric structure. In the ^1H NMR spectrum of **3a** in CD_3OD, the methylene protons of the NHC arms give four sets of broad signals at 5.10, 4.28, 2.87 and 2.68 ppm with an integration ratio of 1:1:1:1, which implies that the methylene protons become diastereotopic due to the loss of free rotation of the NHC arms. In addition, the broadness of these resonances indicates the presence of dynamic behavior in the solution of **3a**. Similar signals were observed as well in the case of **3b** with *N*-phenyl substituents.

The identity of **3a** was unambiguously confirmed using X-ray diffraction analysis of a single crystal



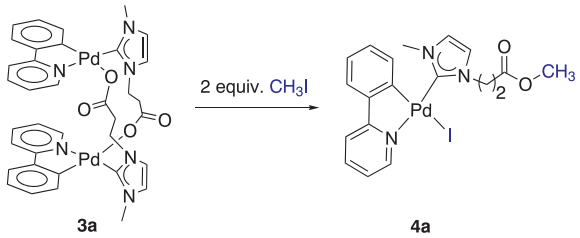
SCHEME 1 Syntheses of carboxylate-NHC bridged dinuclear palladacycles **3a** and **3b**

obtained by slow evaporation of a solution of **3a** in CH_2Cl_2. The molecular structure is depicted in Figure 2. The molecule contains two palladium centers, each of which essentially adopting square planar geometry. The carboxylate-functionalized imidazolin-2-ylidenes serve as the bridges interconnecting two metal centers leading the formation of a 14-membered metallocycle. In addition, the carbene is *cis* to the phenyl donor of [C^N]-chelator, the coordination fashion of which has been observed in some previously reported mononuclear NHC-based palladacycles.[8,9]

2.2 | Esterifications of carboxylate-NHC complexes 3a and 3b

The carboxylate-NHC complexes **3a** and **3b** may serve as potential precursors to access ester- or COOH-functionalized complexes upon esterification or acidolysis. As an initial attempt, **3a** was selected as a representative and treated with CH_3I as electrophile to investigate this reactivity (Scheme 2). Gratifyingly, the reaction proceeded smoothly and afforded ester-anchored complex **4a** in excellent yield.

Such observation prompted us to further expand the scope of alkyl halides (Scheme 3). It was found that alkyl bromides and chlorides can undergo bond scissions cleanly producing a wide range of ester-functionalized NHC palladacycles in good to excellent yields. Note that in the cases of chloro- or



SCHEME 2 Reaction of dinuclear complex **3a** with CH_3I

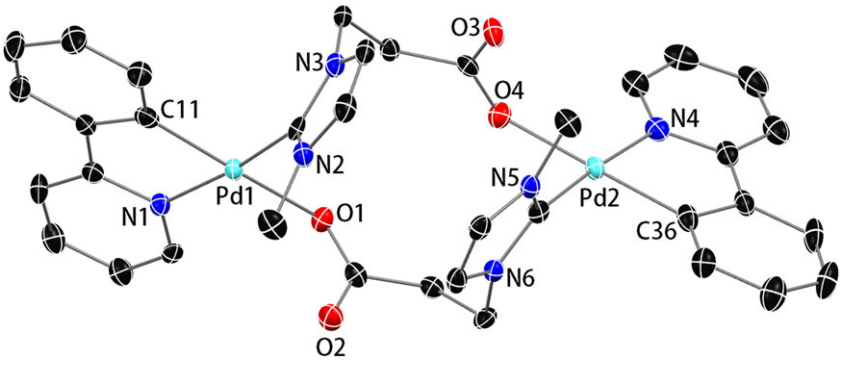
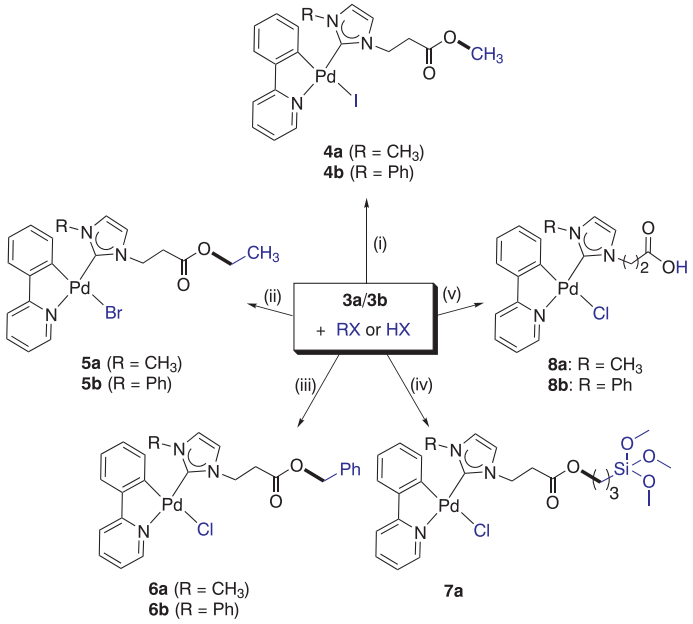


FIGURE 2 Molecular structure of complex **3a** showing 50% probability ellipsoids. Hydrogen atoms and another crystallographically independent molecule have been omitted for clarity



For (i): acetone, excess alkyl halide, 40 °C, 12 h. For (ii)/(iii)/(iv): CH_3CN, excess alkyl halide, 90 °C, 24 h. For (v): CH_2Cl_2, 2 equivalents of HCl, 40 °C, 24 h.

SCHEME 3 Divergent syntheses of ester-/COOH-functionalized NHC palladacycles starting from **3a** or **3b**

bromoalkanes, a more forcing condition (90°C in CH_3CN) needs to be applied to achieve a higher conversion. In all cases, no formation of palladium black was observed.

Additionally, **3a** was used as a representative and treated with (3-chloropropyl)trimethoxysilane. This reaction successfully afforded trimethoxysilyl-functionalized complex **7a** as the product, which can be potentially further grafted onto solid supports such as silica to access heterogeneous catalysts.

For the ester-functionalized complexes **4a**–**7a**, the protons of *N*-ethylene moieties give two sets of complicated multiplets falling in the range 4.57–4.90 and 3.02–3.30 ppm, confirming the presence of geminal couplings brought by the diastereotopic ethylene protons. This suggests that although the carboxylate-NHC bridges of **3a** and **3b** were cleaved, the free rotation of ester-anchored *N*-substituents is restricted. A positive correlation between the rotation barrier and the size of halido coligand has been observed in a previous study.[18] Since **6a** bears the smallest chlorido coligand (versus Br and I), the corresponding rotation barrier is expected to be the lowest. In view of this, **6a** was chosen as a representative and further studied by variable-temperature ^{1}H NMR experiments. It was found that the ethylene signals did not show coalescence even at 353 K, which indicates a high rotation barrier for **6a** and other analogues reported herein. The carbene signals of **4a**–**6b** were found to fall in a narrow range of 173.4–174.6 ppm and the resonances at 172.2–172.8 ppm are assigned to $C_{carbonyl}$ atoms, which were confirmed by 2D HMBC experiments.

Finally, several attempts to use aryl halides to achieve esterification were to no avail even at an elevated reaction temperature, and a non-negligible amount of palladium black was observed.

2.3 | Acidolyses of carboxylate-NHC complexes 3a and 3b

Then, the reactivity of **3a** and **3b** towards hydrochloric acid was examined (Scheme 3). Gratifyingly, when treated with two equivalents of HCl (in aqueous solution), **3a** and **3b** underwent regioselective acidolyses affording COOH-tethered NHC palladacycle **8a** and **8b** as the sole product. Similar to ester-tethered analogues, the *N*-ethylene protons are found to be diastereotopic. The ^{13}C NMR signals of carbonyl group in **8a** and **8b** show significant upfield shift ($\Delta\delta > 7$ ppm) compared to those for ester-functionalized counterparts **4a**–**6b**.

Finally, in all esterification reactions (**4a**–**7a**), no other side reactions occurred despite large excess of alkyl halides being utilized. However, in the cases of acidolysis reactions, **8a** and **8b** can be accessed only when two equivalents of HCl are used. By contrast, in the presence of four equivalents of HCl, the protonation of aryl carbanion was observed as evidenced by the formation of free 2-phenylpyridine in a yield of 48%, which is expected to be formed via the protonation of aryl carbanion followed by ligand dissociation. Finally, in all attempts, no formation of imidazolium salt generated from protonation of carbene was found. This clearly demonstrates the marked

resistance of Pd—$C_{carbene}$ bonds towards acid, which indicates the potential use of such complexes in catalysis especially those requiring acidic conditions (*vide infra*).

Complexes **4a**, **5a**, **6b** and **8b** were further characterized using X-ray diffraction analyses of their single crystals (Figure 3). Selected crystallographic data are listed in Table SI-1 (supporting information). The bite angles ranging from 80.96° to 81.95° are comparable to those reported in non-functionalized[8,9] or functionalized[10] NHC palladacycles. In the solid-state structure of **8b**, it was found that two molecules dimerize through hydrogen bonds, which is similar to the case of acetic acid.[19]

2.4 | Hemilability of functionalities

The ester/COOH functionalities incorporated in the newly synthesized complexes are potentially hemilabile groups. The oxygen atom in the NHC arm may serve as a donor to stabilize an unsaturated metal center, and dissociate in the presence of a stronger incoming ligand. Such behavior is believed to bring stabilization benefits during metal-mediated catalysis.[2,20] As a representative, **4a** was treated with 1 equivalent of $AgBF_4$ as a halide scavenger, and this reaction gave the formation of a tentatively assigned O-coordinated chelating complex **A**[21] as evidenced by ^{1}H NMR spectroscopy (Figure SI-1 in the supporting information). Further addition of NaI as an iodide ligand source cleanly regenerated **4a** demonstrating the revisable coordination–decoordination behavior (hemilability) of the carboxylate-based functionality. This may also account for the exhibited superiority of the functionalized NHC complexes synthesized herein over the non-functionalized counterpart in catalytic reactions (*vide infra*).

2.5 | Catalytic studies

The observed robustness of Pd—$C_{carbene}$ bonds in acidolysis reactions (*vide supra*) encouraged us to examine the catalytic performances of the complexes reported herein in certain reactions under acidic conditions. In a preliminary study, direct aromatic C—H functionalization with alkynes[22] was chosen. In a model reaction, mesitylene (**9**) and ethyl propiolate (**10**) were employed as the substrates, and trifluoroacetic acid was used as the solvent (Table 1). In the very first attempt, the hydroarylation reaction was carried out at 60°C affording ethyl (*Z*)-2,4,6-trimethylphenylacrylate (**11**) and the bis addition product **12** in a total yield of 84% (entry 1). This reaction was found to proceed smoothly at a milder condition (at 25°C) but for a prolonged time, which can also give a comparable yield and selectivity.

Under this condition, all other ester- or COOH-functionalized palladacyclic complexes were subjected to

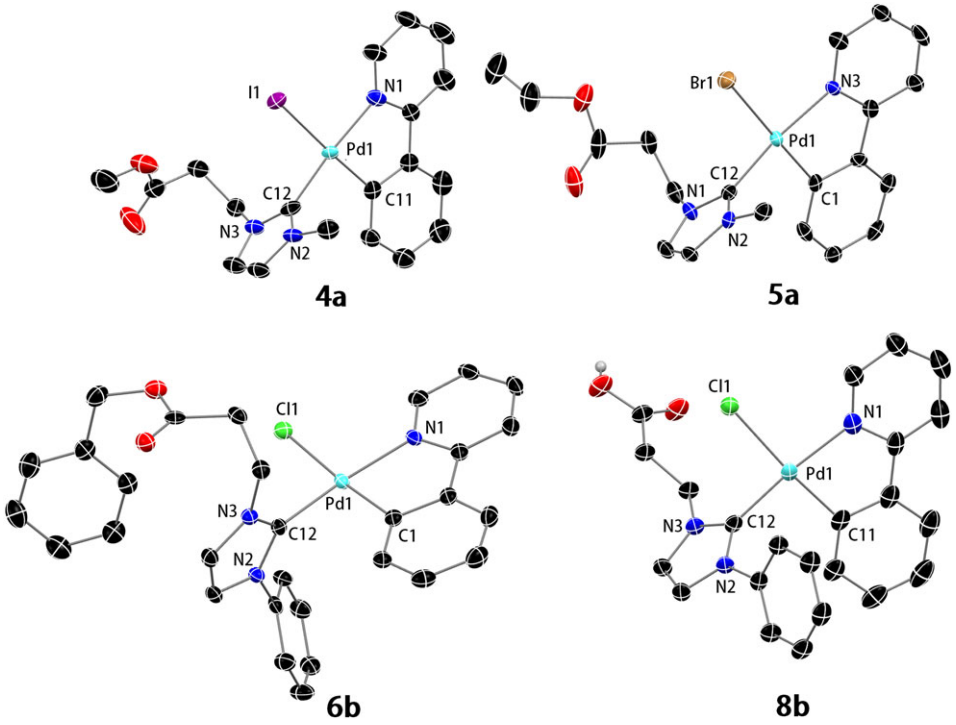
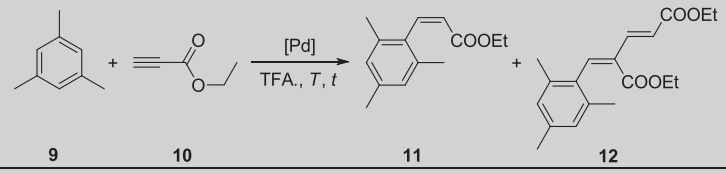


FIGURE 3 Molecular structures of complexes **4a**, **5a**, **6b** and **8b** showing 50% probability ellipsoids. Hydrogen atoms (except for COOH hydrogen in **8b**), solvent molecules, another crystallographically independent molecule (for **4a**) and the disordered ethyl group (for **5a**) have been omitted for clarity

TABLE 1 Hydroarylation of ethyl propiolate (**10**) with mesitylene (**9**)[a]



9 10 11 12

Entry	Cat.	Cat. loading (%)	Temp. (°C)	Time (h)	Poisoning agent	Yield (%)[b] Total	11	12
1	**3a**	0.5	60	2	—	86	54	32
2	**3a**	0.5	25	24	—	88	58	30
3	**3b**	0.5	25	24	—	82	50	32
4	**4a**	1	25	24	—	82	62	20
5[c]	**4a**	1	25	24	Hg	84	64	20
6[d]	**4a**	1	25	24	PPh_3	65	53	12
7	**4b**	1	25	24	—	67	55	12
8	**5a**	1	25	24	—	88	61	27
9	**5b**	1	25	24	—	86	61	25
10	**6a**	1	25	24	—	88	61	27
11	**6b**	1	25	24	—	80	60	20
12	**8a**	1	25	24	—	95	60	35
13	**8b**	1	25	24	—	92	61	30

[a]Reaction conditions: (i) 1.5 mmol of mesitylene (**9**), 1.0 mmol of ethyl propiolate (**10**), 1 mol% (for mononuclear complexes) or 0.5 mol% (for dinuclear complexes) of precatalyst, trifluoroacetic acid (1 ml).

[b]Yields (with respect to ethyl propiolate) were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxylbenzene as an internal standard.

[c]Two drops of mercury were added into the reaction tube after 1 h.

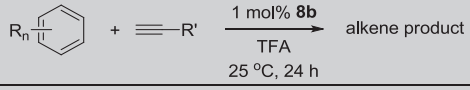
[d]0.0003 mmol (3% with respect to catalyst loading) of PPh_3 was added into the reaction tube after 1 h.

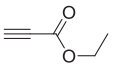
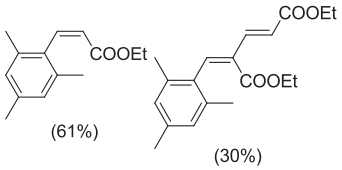
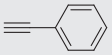
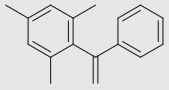
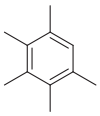
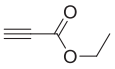
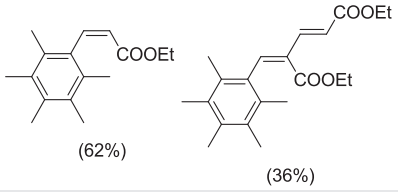
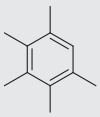
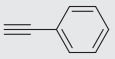
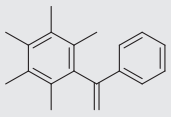
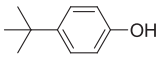
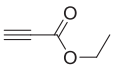
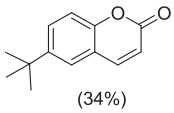
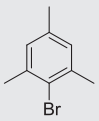
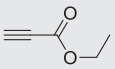
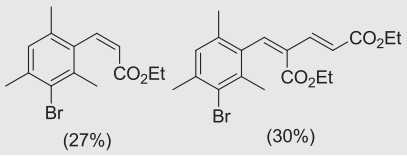
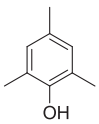
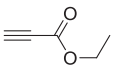
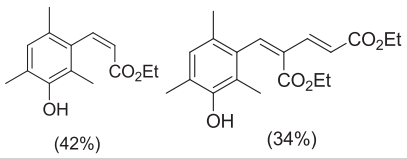
this hydroarylation reaction, revealing the good performances of all precatalysts. The highest selectivity was observed in the cases of iodido complexes **4a** and **4b**, the reason for which is currently not clear yet. Additionally, complexes bearing NHCs with *N*-methyl substituents are generally slightly superior to or comparable with their counterparts with *N*-phenyl substituents (e.g. entry 10 versus entry 11). It should be additionally noted that under an acidic condition, the ester groups of the precatalysts may undergo acidolyses generating structurally similar species.[13b] This may account for the small differences of catalytic activities for most complexes.

The hemilability of carboxylate-based functionalities in the NHC arms may bring potential benefits to the catalytic reactions (*vide supra*). To give a deeper insight, a non-functionalized NHC counterpart [PdI(C^N)(^{Ph,Bu}imy)] (C^*N* = 2-(2-pyridinyl)phenyl-*C*,*N*, ^{Ph,Bu}imy = 1-phenyl-4-^{n}butylimdazolin-2-ylidene; **B**) was used to make a comparison with its structurally comparable analogue **4b**. The former precatalyst gives the formation of the product **11** as the predominant product in a yield of 40% (2 h), while the yield can reach 53% in the case with **4b** as the precatalyst. The superior catalytic behavior of the latter is tentatively attributed to the positive effects brought by the oxygen-containing functionality, which remains to be further investigated in greater detail in future.

In addition, a few poisoning experiments were carried out to distinguish the homogeneity/heterogeneity of the present catalytic system. Elemental mercury[23] is known to stall or markedly undermine catalytic activity if the palladium-mediated reaction is heterogeneously catalyzed. As a supplementary experiment, 3 mol% (with respect to the catalyst) of PPh_3 was also applied as a poisoning agent. This method, although less widely used compared to Hg poisoning, was proposed by Widegren and Finke[24] and has been used by some others.[25] It has been suggested that only a few active metal sites on the surface of a heterogeneous catalyst can be sufficiently poisoned by <<1.0 equivalent (with respect to the catalyst) of a ligand such as PPh_3. It was found that no sharp drop of yield was observed for the catalysis in the presence of these poisoning agents (entries 4–6), which indicates the hydroarylation reactions are likely to be homogeneously catalyzed.

TABLE 2 Hydroarylation of alkynes with **8b** as precatalyst[a]



Entry	Arene	Alkyne	Product (yield, %)
1			 (61%) (30%)
2			 (53%)
3			 (62%) (36%)
4			 (52%)
5			 (34%)
6			 (27%) (30%)
7			 (42%) (34%)

[a]Reaction conditions: (i) 1.5 mmol of mesitylene (**9**), 1.0 mmol of ethyl propiolate (**10**), 1 mol% of **8b**, trifluoroacetic acid (1 ml), 25°C, 24 h.

[b]Yields (with respect to ethyl propiolate) were determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxylbenzene as an internal standard.

With **8b** as the representative precatalyst, a selection of electronically and sterically varied alkynes and arenes were employed to further expand the substrate scope (Table 2). When employing ethyl propiolate as the alkyne substrate, good yields can be obtained in both cases of mesitylene or pentamethylbenzene (entries 1 and 3). However, moderate yields were observed when a more challenging alkyne substrate, phenylacetylene, was used (entries 2 and 4). To further investigate the functionality tolerance, arene substrates with various functional groups (e.g. Br, OH) were employed, and the catalytic reactions gave the desired products in moderate yields (entries 5–7). In a particular case also accompanying a cyclization process, a lactone product can be achieved in a low yield of 34% (entry 5).

3 | CONCLUSIONS

In summary, this study reports two dinuclear palladacyclic complexes, which bear carboxylate-tethered NHC ligands adopting bridging modes. These complexes proved to be suitable precursors to access carboxylic acid-/ester-functionalized NHC palladacycles in a

divergent and expedient manner. No side reactions involving aryl-based carbanions occurred in the cases of esterification even when excess aryl halide is employed, while the reactivity in acidolysis reactions is found to be dependent on the amount of HCl used. Finally and in a preliminary study, all complexes are found to exhibit good catalytic behaviors in direct aromatic C—H functionalizations with alkynes. The superior catalytic performance exhibited by the df-NHC complex over its non-functionalized counterpart has been tentatively attributed to the hemilability of the carboxylate-based NHC substituents. Poisoning experiments with Hg or PPh_3 suggest a homogeneous nature of the catalytic system.

This report provides a series of new examples of less studied df-NHC-containing palladacycles. To the best of our knowledge, this is also the first report demonstrating that esterification/acidolysis of NHC arms can be achieved without affecting palladacyclic motifs. The divergent synthetic route and catalytic studies explored herein will facilitate the syntheses and applications of NHC palladacycles and related complexes. Further expanding the structural diversity of target complexes and the substrate scope of catalytic hydroarylations is currently underway in our laboratory.

4 | EXPERIMENTAL

4.1 | General considerations

Unless otherwise stated, all the manipulations were carried out without taking precautions to exclude air and moisture. All chemicals and solvents were used as received without further purification if not mentioned otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian 600 MHz spectrometer at Capital Normal University, a Bruker 400 MHz spectrometer at Beijing University of Chemical Technology, or a Bruker 700 MHz spectrometer at Beijing Institute of Technology. The chemical shifts were internally referenced to the residual solvent signals relative to $(CH_3)_4Si$ (^{1}H, ^{13}C). ESI mass spectra were measured using an Agilent 6540 Q-TOF mass spectrometer at Beijing University of Chemical Technology. X-ray single crystal diffraction analyses were done using a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer at Beijing Normal University or a Rigaku XtaLAB P200 MM003 diffractometer at Capital Normal University or an Agilent Xcalibur Eos Gemini diffractometer at Beijing University of Chemical Technology. Elemental analyses were done with a Vario EL cube elemental analyzer at Beijing University of Chemical Technology.

4.2 | Synthesis of 1b

A 25 ml Schlenk tube was charged with 1-phenylimidazole (506 μl, 4.0 mmol), 3-chloroproionic acid (446 mg, 4.1 mmol) and toluene (5 ml). The reaction mixture was heated under reflux for 12 h. After cooling to ambient temperature, the precipitate was collected by centrifugation and washed with ethyl acetate (3 ml × 5). The residue was fully dried under vacuum affording the product as a white solid in a yield of 86%. ^{1}H NMR (DMSO-d_6, 600 MHz, δ, ppm): 12.74 (s, 1H, COOH), 9.97 (s, 1H, NCN), 8.34 (s, 1H, Ar—H), 8.05 (s, 1H, Ar—H), 7.81–7.79 (m, 2H, Ar—H), 7.68–7.66 (m, 2H, Ar—H), 7.60–7.58 (m, 1H, Ar—H), 4.46 (t, 2H, NCH_2, J = 6.6 Hz), 3.03 (s, 2H, NCH_2CH_2, J = 6.6 Hz). ^{13}C NMR (DMSO-d_6, 175 MHz, δ, ppm): 171.6 (C═O), 136.0, 134.7, 130.2, 129.6, 123.6, 121.6, 120.7 (Ar—C), 45.2 (NCH_2), 33.8 (NCH_2CH_2).

4.3 | General procedure for syntheses of 3a and 3b

A 25 ml Schlenk tube was charged with compound **2** (0.5 mmol, 320 mg) and imidazolium salt (1.0 mmol). Then, K_2CO_3 (5 mmol, 690 mg) and CH_3CN (5 ml) were added. The reaction mixture was heated for 24 h at 100°C. All the volatiles were removed under vacuum yielding a yellow solid. The desired product was extracted using CH_2Cl_2 (3 ml × 3) and purified using column chromatography (SiO_2).

Complex **3a** was obtained as a pale yellow solid in a yield of 78%. ^{1}H NMR (CD_3OD, 600 MHz, δ, ppm): 8.58 (br s, 2H, Pyr—H), 7.94–7.88 (m, 4H, Ar—H), 7.62 (d, 2H, Ar—H, J = 7.2 Hz), 7.32–7.25 (m, 6H, Ar—H), 7.06–7.04 (m, 2H, Ar—H), 6.91 (t, 2H, Ar—H, J = 7.8 Hz), 6.52 (br s, 2H, Ar—H), 5.10, 4.28 (br s, 4H, NCH_2), 3.86 (s, 6H, NCH_3), 2.87, 2.68 (br s, 4H, NCH_2CH_2). MS (ESI) m/z 414 $[M/2 + H]^+$. Anal. Calcd for $C_{36}H_{34}N_6O_4Pd_2$ (%): C, 52.25; H, 4.14; N, 10.16. Found (%): C, 51.97; H, 4.36; N, 10.38.

Complex **3b** was obtained as a pale yellow solid in a yield of 72%. ^{1}H NMR (CD_3OD, 600 MHz, δ, ppm): 8.69 (br s, 2H, Pyr—H), 8.04–8.03 (m, 4H, Ar—H), 7.96–7.93 (m, 2H, Ar—H), 7.84–7.82 (m, 2H, Ar—H), 7.68 (s, 2H, Ar—H), 7.58 (s, 2H, Ar—H), 7.45–7.44 (m, 3H, Ar—H), 7.36–7.34 (m, 5H, Ar—H), 7.26–7.24 (m, 2H, Ar—H), 6.85–6.83 (m, 2H, Ar—H), 6.57 (br s, 2H, Ar—H), 6.33 (br s, 2H, Ar—H), 5.46, 4.39 (br s, 4H, NCH_2), 2.92–2.89 (m, 2H, NCH_2CH_2), 2.80–2.75 (m, 2H, NCH_2CH_2). MS (ESI) m/z 476 $[M/2 + H]^+$. Anal. Calcd for $C_{46}H_{38}N_6O_4Pd_2$ (%): C, 58.05; H, 4.02; N, 8.83. Found (%): C, 57.88; H, 3.95; N, 8.46.

4.4 | General procedure for syntheses of 4a and 4b

A 25 ml Schlenk tube was charged with compound **3a** or **3b** (0.02 mmol) and acetone (1 ml). To this mixture, CH_3I (0.6 mmol) was added. Then the reaction mixture was stirred for 12 h at 40°C. All the volatiles were evaporated under vacuum, and the crude product was washed with diethyl ether (1 ml × 3). The residue was fully dried under vacuum affording the product as a yellow solid.

Complex **4a** was obtained in a yield of 99%.[1] H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.70 (s, 1H, Pyr—H), 7.80–7.72 (m, 2H, Ar—H), 7.56–7.55 (m, 1H, Ar—H), 7.19–7.18 (m, 2H, Ar—H), 7.09–7.07 (m, 1H, Ar—H), 6.99–6.98 (m, 1H, Ar—H), 6.94–6.91 (m, 1H, Ar—H), 5.92 (d, 1H, Ar—H, J = 6.0 Hz), 4.65–4.57(m, 2H, NCH_2), 3.88 (s, 3H, NCH_3), 3.62 (s, 3H, OCH_3), 3.13–3.03 (m, 2H, NCH_2CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 173.4 (NCN), 172.7 (C═O), 164.8, 157.8, 154.7, 147.4, 138.8, 136.0, 130.5, 125.0, 124.5, 123.5, 123.2, 122.8, 119.0 (Ar—C), 52.5 (OCH_3), 47.3 (NCH_2), 39.4 (NCH_3), 35.2 (NCH_2CH_2). MS (ESI): m/z 428 $[M - I]^+$. Anal. Calcd for $C_{19}H_{20}IN_3O_2Pd$ (%): C, 41.07; H, 3.63; N, 7.56. Found (%): C, 41.02; H, 3.75; N, 7.28.

Complex **4b** was obtained in a yield of 98%. ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.68 (d, 1H, Pyr—H, J = 6 Hz), 7.93 (d, 2H, Ar—H, J = 12 Hz), 7.72 (t, 1H, Ar—H, J = 6 Hz), 7.64–7.62 (m, 1H, Ar—H), 7.46 (d, 1H, Ar—H, J = 6 Hz), 7.40 (s, 1H, Ar—H), 7.36–7.34 (m, 2H, Ar—H), 7.28–7.27 (m, 2H, Ar—H), 7.11 (t, 1H, Ar—H, J = 6.0 Hz), 7.03 (t, 1H, Ar—H, J = 6.0 Hz), 6.91 (t, 1H, Ar—H, J = 6.0 Hz), 6.03 (d, 1H, Ar—H, J = 6.0 Hz), 4.88–4.81 (m, 1H, NCH_2), 4.76–4.72 (m, 1H, NCH_2), 3.65 (s, 3H, OCH_3), 3.24–3.19 (m, 1H, NCH_2CH_2), 3.14–3.10 (m, 1H, NCH_2CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 173.6 (NCN), 172.8 (C═O), 164.9, 157.9, 154.9, 147.1, 140.8, 138.7, 136.2, 130.3, 129.7, 128.8, 125.9, 124.8, 124.3, 124.0, 123.3, 122.9, 118.9 (Ar—C), 52.5 (OCH_3), 47.9 (NCH_2), 35.0 (NCH_2CH_2). MS (ESI): m/z 490 $[M - I]^+$. Anal. Calcd for $C_{24}H_{22}IN_3O_2Pd$ (%): C, 46.66; H, 3.59; N, 6.80. Found (%): C, 46.42; H, 3.78; N, 6.47.

4.5 | General procedure for syntheses of 5a and 5b

A 25 ml Schlenk tube was charged with compound **3a** or **3b** (0.02 mmol) and CH_3CN (1 ml). To this mixture, CH_3CH_2Br (0.6 mmol) was added. Then the reaction mixture was stirred for 24 h at 90°C. All the volatiles were evaporated under vacuum, and the crude product was washed with diethyl ether (1 ml × 3). The residue was fully dried under vacuum affording the product.

Complex **5a** was obtained as a pale yellow solid in a yield of 96%. ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.48 (dd, 1H,J_1 = 6.6 Hz, J_2 = 1.2 Hz, Pyr—H), 7.81 (td, 1H, J_1 = 1.8 Hz, J_2 = 7.8 Hz, Ar—H), 7.73–7.71 (m, 1H, Ar—H), 7.56 (dd, 1H, J_1 = 0.6 Hz, J_2 = 7.8 Hz, Ar—H), 7.22–7.19 (m, 2H, Ar—H), 7.19 (d, 1H, J = 1.8 Hz, Ar—H), 7.08 (td, 1H, J_1 = 7.2 Hz, J_2 = 0.6 Hz, Ar—H), 6.97 (d, 1H, J = 1.8 Hz, Ar—H), 6.90 (td, 1H, J_1 = 7.8 Hz, J_2 = 1.2 Hz, Ar—H), 6.02 (d, 1H, J = 7.2 Hz, Ar—H), 4.70–4.61 (m, 2H, NCH_2), 4.09 (q, 2H, J = 6.0 Hz, OCH_2), 3.94 (s, 3H, NCH_3), 3.14–3.02 (m, 2H, NCH_2CH_2), 1.19 (t, 3H, J = 7.2 Hz, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 174.1 (NCN), 172.4 (C═O), 164.9, 156.2, 151.8, 147.3, 139.1, 136.7, 130.5, 124.9, 124.4, 123.2, 123.1, 122.6, 118.7 (Ar—C), 61.4 (OCH_2), 47.3 (NCH_2), 39.3 (NCH_3), 35.9 (NCH_2CH_2), 14.8 (OCH_2CH_3). MS (ESI) m/z 442 $[M - I]^+$. Anal. Calcd for $C_{20}H_{22}BrN_3O_2Pd$ (%): C, 45.95; H, 4.24; N, 8.04. Found (%): C, 45.72; H, 4.56; N, 8.38.

Complex **5b** was obtained as a pale yellow solid in a yield of 90%. ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.45 (s, 1H, Pyr—H), 7.97–7.96 (m, 2H, Ar—H), 7.72 (s, 1H, Ar—H), 7.60 (s, 1H, Ar—H), 7.40–7.26 (m, 6H, Ar—H), 7.14 (s, 1H, Ar—H), 6.98 (s, 1H, Ar—H), 6.84 (s, 1H, Ar—H), 6.03 (s, 1H, Ar—H), 4.85, 4.77 (br s, 2H, NCH_2), 4.10 (br s, 2H, OCH_2CH_3), 3.19, 3.13 (br s, 2H, NCH_2CH_2), 1.20 (br s, 3H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 174.2 (NCN), 172.5 (C═O), 164.9, 156.3, 151.9, 146.9, 140.8, 138.9, 136.7, 130.2, 129.7, 128.7, 125.8, 124.6, 124.2, 124.0, 122.9, 122.5, 118.6 (Ar—C), 61.5 (OCH_2), 47.8 (NCH_2), 35.6 (NCH_2CH_2), 14.8 (OCH_2CH_3). MS (ESI) m/z 504 $[M - I]^+$. Anal. Calcd for $C_{25}H_{24}BrN_3O_2Pd$ (%): C, 51.35; H, 4.14%; N, 7.19%. Found (%): C, 51.16%; H, 4.56%; N, 6.93%.

4.6 | General procedure for the syntheses of 6a and 6b

A 25 ml Schlenk tube was charged with compound **3a** or **3b** (0.02 mmol) and CH_3CN (1 ml). To this mixture, $PhCH_2Cl$ (0.6 mmol) was added. Then the reaction mixture was stirred for 24 h at 90°C. All the volatiles were evaporated under vacuum, and the crude product was washed with diethyl ether (1 ml × 3). The residue was fully dried under vacuum affording the product as a pale yellow solid.

Complex **6a** was obtained in a yield of 93%. ^1H NMR ($CDCl_3$, 700 MHz, δ, ppm): 9.36 (s, 1H, Pyr—H), 7.85–7.84 (m, 1H, Ar—H), 7.76–7.75 (m, 1H, Ar—H), 7.60–7.59 (m, 1H, Ar—H), 7.36–7.26 (m, 6H, Ar—H), 7.17 (s, 1H, Ar—H), 7.10–7.08 (m, 1H, Ar—H), 6.98 (s, 1H, Ar—H), 6.89–6.88 (m, 1H, Ar—H), 6.10 (d, 1H, J = 7.0 Hz, Ar—H), 5.12, 5.09 (d, 2H, J = 12.0 Hz, OCH_2Ph), 4.78–4.69 (m,

2H, NCH_2CH_2), 3.99 (s, 3H, NCH_3), 3.24–3.14 (m, 2H, NCH_2CH_2). ^{13}C NMR ($CDCl_3$, 175 MHz, δ, ppm): 174.5 (NCN), 172.2 (C═O), 164.8, 155.2, 150.3, 147.3, 139.2, 137.1, 136.2, 130.5, 129.2, 128.9, 124.8, 124.4, 123.2, 122.8, 122.5, 118.6 (Ar—C), 67.2 (OCH_2Ph), 47.2 (NCH_2), 39.2 (NCH_3), 36.2 (NCH_2CH_2). MS (ESI): *m/z* 504 $[M - Cl]^+$. Anal. Calcd for $C_{25}H_{24}ClN_3O_2Pd$ (%): C, 55.57; H, 4.48; N, 7.78. Found (%): C, 55.09; H, 4.18; N, 7.45.

Complex **6b** was obtained in a yield of 91%. ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.28 (d, 1H, J = 4.0 Hz, Pyr—H), 7.97 (d, 2H, J = 7.6 Hz, Ar—H), 7.67 (td, 1H, J_1 = 1.2 Hz, J_2 = 7.6 Hz, Ar—H), 7.53 (m, 1H, Ar—H), 7.34–7.26 (m, 9H, Ar—H), 7.23–7.20 (m, 2H, Ar—H), 7.13–7.10 (m, 1H, Ar—H), 6.91 (t, 1H, J = 7.2 Hz, Ar—H), 6.75 (td, 1H, J_1 = 0.8 Hz, J_2 = 7.6 Hz, Ar—H), 6.02 (d, 1H, J = 7.2 Hz, Ar—H), 5.11, 5.05 (d, 2H, $^2J_{H,H}$ = 12.4 Hz, OCH_2), 4.90–4.74 (NCH_2), 3.30–3.16 (m, 2H, NCH_2CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 174.6 (NCN), 172.3 (C═O), 164.8, 155.3, 150.3, 146.8, 140.7, 139.0, 136.9, 136.2, 130.1, 129.7, 129.1, 128.8, 128.7, 125.6, 124.4, 124.1, 124.0, 122.5, 122.2, 118.5 (Ar—C), 67.1 (OCH_2), 47.7 (NCH_2), 35.8 (NCH_2CH_2). MS (ESI) *m/z* 566 $[M - Cl]^+$. Anal. Calcd for $C_{30}H_{26}ClN_3O_2Pd$ (%): C, 59.81; H, 4.35; N, 6.98. Found (%): C, 59.45; H, 4.14; N, 7.40.

4.7 | Synthesis of 7a

Complex **3a** (0.1 mmol, 82.7 mg), (3-choloropropyl) trimethoxysilane (1.6 mmol, 296 μl) and CH_3CN were mixed in a Schlenk tube under nitrogen atmosphere. The tube was sealed and the reaction mixture was stirred and heated under reflux for 24 h. All the volatiles were evaporated under vacuum. The obtained yellow residue was purified using column chromatography (SiO_2) affording the product as a pale yellow solid in a yield of 20%. ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.31–9.30 (m, 1H, Ar—H), 7.80 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.8 Hz, Ar—H), 7.71–7.70 (m, 1H, Ar—H), 7.54 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.2 Hz), 7.22–7.18 (m, 2H, Ar—H), 7.05 (td, 1H, J_1 = 7.8 Hz, J_2 = 0.6 Hz, Ar—H), 6.96–6.95 (m, 1H, Ar—H), 6.88 (td, 1H, J_1 = 7.8 Hz, J_2 = 1.2 Hz, Ar—H), 6.05–6.04 (m, 1H, Ar—H), 4.71–4.61(m, 2H, NCH_2), 3.98 (t, 2H, J = 6.6 Hz, OCH_2), 3.94 (s, 3H, NCH_3), 3.53 (s, 9H, $SiOCH_3$), 3.13–3.02 (m, 2H, NCH_2CH_2), 1.69–1.64 (m, 2H, $OCH_2CH_2CH_2$), 0.60–0.56 (m, 2H, $OCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 174.5 (NCN), 172.4 (C═O), 164.8, 155.2, 150.3, 147.2, 139.2, 137.0, 130.4, 124.8, 123.2, 122.8, 122.5, 118.6 (Ar—C), 67.3 (OCH_2), 51.2 ($SiOCH_3$), 47.2 (NCH_2), 39.2 (NCH_3), 36.1 (NCH_2CH_2), 22.5 (OCH_2CH_2), 5.9 ($OCH_2CH_2CH_2$). MS (ESI): *m/z* 576 $[M - Cl]^+$. Anal. Calcd for $C_{24}H_{32}ClN_3O_5PdSi$ (%): C, 47.06; H, 5.27; N, 6.86. Found (%): C, 46.75; H, 5.14; N, 6.71.

4.8 | General procedure for syntheses of 8a and 8b

A 25 ml Schlenk tube was charged with **3a** or **3b** (0.06 mmol) and CH_2Cl_2 (3 ml). To this mixture, an aqueous solution of HCl (0.12 mmol) was added. The mixture was stirred at 40°C for 24 h. All the volatiles were evaporated under vacuum affording the product as a bright yellow solid.

Complex **8a** was obtained in a yield of 96%. ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.19 (br s, 1H, Pyr—H), 7.80–7.77 (m, 1H, Ar—H), 7.69–7.68 (m, 1H, Ar—H), 7.53 (d, 1H, J = 7.8 Hz, Ar—H), 7.20–7.18 (m, 1H, Ar—H), 7.14 (br s, 1H, Ar—H), 7.05–7.02 (m, 1H, Ar—H), 6.96–6.95 (m, 1H, Ar—H), 6.89–6.86 (m, 1H, Ar—H), 6.07 (br s, 1H, Ar—H), 4.63, 4.53 (br s, 2H, NCH_2), 3.90 (s, 3H, NCH_3), 3.14–3.10, 2.96–2.94 (m, 2H, NCH_2CH_2). The signal of COOH proton was not observed. ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 173.9 (NCN), 164.6 (C═O), 150.0, 147.1, 139.3, 137.2, 130.5, 124.9, 124.4, 123.0, 122.9, 122.8, 118.7 (Ar—C), 54.1 (NCH_2), 47.4 (NCH_2CH_2), 39.1 (NCH_3). MS (ESI): *m/z* 414 $[M - Cl]^+$. Anal. Calcd for $C_{18}H_{18}ClN_3O_2Pd$ (%): C, 48.02; H, 4.03; N, 9.33. Found (%): C, 47.78; H, 4.34; N, 8.91.

Complex **8b** was obtained in a yield of 92%.^1H NMR (DMSO-d_6, 600 MHz, δ, ppm): 9.14 (d, 1H, J = 5.4 Hz, Pyr—H), 8.09–8.08 (m, 2H, Ar—H), 8.00–7.97 (m, 2H, Ar—H), 7.84 (s, 1H, Ar—H), 7.72 (s, 1H, Ar—H), 7.65–7.63 (m, 1H, Ar—H), 7.45–7.41 (m, 3H, Ar—H), 7.31 (t, 1H, J = 7.2 Hz, Ar—H), 6.96 (t, 1H, J = 7.2 Hz, Ar—H), 6.82 (t, 1H, J = 7.2 Hz, Ar—H), 5.96 (d, 1H, J = 7.2 Hz, Ar—H), 4.67–4.58 (m, 2H, NCH_2), 3.01, 2.94 (br s, 2H, NCH_2CH_2). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 171.8 (NCN), 163.7 (C═O), 154.6, 148.8, 145.9, 139.9, 139.6, 135.9, 129.7, 129.0, 127.8, 124.5, 124.0, 123.9, 123.4, 122.6, 122.5, 118.8 (Ar—C), 54.9 (NCH_2, NCH_2CH_2). MS (ESI): *m/z* 476 $[M - Cl]^+$. Anal. Calcd for $C_{23}H_{20}ClN_3O_2Pd$ (%): C, 53.92; H, 3.93; N, 8.20. Found (%): C, 53.83; H, 4.16; N, 8.51.

4.9 | Synthesis of B

Complex **B** was synthesized by treating compound **2** with 1-phenyl-3-^{n}butylimidazolium iodide salt and K_2CO_3 following a procedure similar to that for accessing **3a** and **3b**. Complex **B** was obtained as a yellow solid in a yield of 70%. ^1H NMR ($CDCl_3$, 600 MHz, δ, ppm): 9.67 (dd, 1H, Pyr—H, J_1 = 5.4 Hz, J_2 = 0.6 Hz), 7.95–7.93 (m, 2H,

Ar—H), 7.66 (td, 1H, Ar—H, J_1 = 7.8 Hz, J_2 = 1.2 Hz), 7.57–7.56 (m, 1H, Ar—H), 7.40 (dd, 1H, Ar—H, J_1 = 7.8 Hz, J_2 = 1.2 Hz), 7.33–7.28 (m, 3H, Ar—H), 7.24–7.21 (m, 1H, Ar—H), 7.18 (d, 1H, Ar—H, J = 2.6 Hz), 7.07–7.04 (m, 1H, Ar—H), 6.99 (td, 1H, Ar—H, J_1 = 7.8 Hz, J_2 = 1.2 Hz), 6.89 (dd, 1H, Ar—H, J_1 = 7.8 Hz, J_2 = 1.8 Hz), 6.08 (dd, 1H, Ar—H, J_1 = 7.2 Hz, J_2 = 0.6 Hz), 4.61–4.57 (m, 1H, NCH_2), 4.39–4.34 (m, 1H, NCH_2), 2.04–1.96 (m, 1H, NCH_2CH_2), 1.89–1.81 (m, 1H, NCH_2CH_2), 1.40–1.31 (m, 2H, $NCH_2CH_2CH_2$), 0.85 (t, 3H, $NCH_2CH_2CH_2CH_3$, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz, δ, ppm): 172.9 (NCN), 164.7, 158.0, 154.8, 147.0, 140.8, 138.6, 136.3, 130.1, 129.5, 128.6, 125.8, 124.6, 124.2, 123.2, 122.9, 122.3, 118.8 (Ar—C), 52.5 (NCH_2), 32.3 (NCH_2CH_2), 20.6 ($NCH_2CH_2CH_2$), 14.3 ($NCH_2CH_2CH_2CH_3$). MS (ESI): *m/z* 460 $[M - I]^+$. Anal. Calcd for $C_{46}H_{38}N_6O_4Pd_2$ (%): C, 49.04; H, 4.12; N, 7.15. Found (%): C, 48.76; H, 3.88; N, 7.55.

4.10 | General procedure for catalytic hydroarylations

A 25 ml Schlenk tube was charged with precatalyst (0.01 mmol for mononuclear complex and 0.005 mmol for dinuclear complex) and a magnetic stirrer. Then, mesitylene (1.5 mmol, 208 μl), ethyl propiolate (1.0 mmol, 101 μl) and trifluoroacetic acid (1000 μl) were added. The tube was sealed and the reaction mixture was stirred at the temperature indicated in Table 1. CH_2Cl_2 (5 ml) and deionized water (5 ml) were added. The organic phase was washed with water (5 ml × 3) and collected. 1,3,5-Trimethoxylbenzene (1.0 mmol) as an internal standard was added. All the volatiles were removed *in vacuo*, and the crude product was analyzed by ^{1}H NMR spectroscopy.

4.11 | X-ray diffraction studies

Structural solution was carried out with the Olex2 program.[26] The structure was solved using direct methods. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. All hydrogen atoms were put at calculated positions. A summary of selected important crystallographic data is given in Table SI-1 (supporting information). CCDC 1847062 and 1847064–1847067 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.

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CONFLICT OF INTEREST

There are no conflicts to declare.

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