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Tetranuclear Palladium Complexes of Abnormal *N*-Heterocyclic Carbene Ligands and their Catalytic Activities in Mizoroki-Heck Coupling Reaction of Electron-Rich Aryl Chlorides

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Abstract. Based on the ligand scaffold of an imidazolyl/benziimidazolyl moiety and a *N*-$CH_2C(=O)NHPh$ substituent, two series of ligand precursors with *ortho* hydroxy groups incorporated on the *N*-phenyl rings were prepared. The structural fine tuning of the ligand scaffold allowed the synthesis of tetranuclear palladium complexes with abnormal *N*-heterocyclic carbene (*a*NHC) ligands. For precursors with C2-methyl blocking groups, pyridine-assisted C—H bond activation led to the formation of mononuclear tridentate palladium *a*NHC complexes or tetranuclear complexes with tridentate CNO donors. Representative mononuclear and tetranuclear palladium *a*NHC complexes were structurally characterized by X-ray diffraction studies, revealing very short Pd─C bond distances. The tetranuclear palladium *a*NHC complexes were very effective in catalyzing Mizoroki-Heck coupling reaction, and were capable of employing a range of aryl chlorides including deactivated substrates with low palladium loading of 0.2 mol%.

Keywords: Carbene ligands; Palladium; C—C coupling; Heck reaction; Tridentate ligands

Introduction

Mononuclear palladium complexes are ubiquitous in the literature because of their numerous catalytic applications in synthetic organic chemistry.[1] In particular, monopalladium complexes with *N*-heterocyclic carbene (NHC) ligands have proved highly versatile in the last two decades for catalyzing various cross-coupling reactions.[2] Because of the recent interest in supramolecular coordination complexes (SCC), the chemistry of multinuclear palladium complexes has attracted significant attention.[3] Nevertheless, tetranuclear palladium complexes are rarely used in cross-coupling reactions.[4] Huynh et al. investigated the catalytic activity of a tetranuclear $[Pd_4S_4]$ macrocyclic square based on NHC ligand in aqueous Suzuki-Miyaura coupling reaction.[4a] A series of dendritic palladium catalysts including a soluble tetranuclear complex, some of which were effective in catalyzing various cross-coupling reactions, were reported by Astruc et al.[4b] Song and Yin reported that tetranuclear palladium complexes containing *C*,*N*-bidentate furoylhydrazone exhibited good activity in Suzuki-Miyaura coupling reaction of activated aryl chlorides.[4d] Knölker et al. found that several tetranuclear palladium complexes obtained from the metalation of dimethyaminoarene derivatives showed excellent catalytic activities with high turnover number (TON) and high turnover frequencies (TOF) in cross-coupling reactions of aryl bromides at room temperature.[4e] However, the use of unreactive aryl chlorides was not reported.

It has been shown that imidazole-based NHC ligands can have alternative binding modes via C4/5 atoms, instead of the commonly observed coordination via the C2 atom. These variants of NHC ligands are called "abnormal NHCs (*a*NHCs)".[5] Because they are more electron-rich than their normal counterparts,[5a,6] improved catalytic activities have been reported.[6d,6e,7] Considering this information, we reasoned that tetranuclear palladium complexes featuring *a*NHC ligands as catalysts in cross-coupling reactions would be worthy of investigation. To our knowledge, these kinds of complexes are still unknown in the literature. Previously, we reported various palladium(II) complexes with a ligand scaffold bearing an imidazolyl moiety and a *N*-$CH_2C(=O)NRPh$ sidearm (R = H or Me) (Figure 1).[8] The ligand scaffold possesses various sites that may undergo C–H or N–H cleavage, resulting in different palladium complexes. These include *C*,*C*-type palladacycle **A** and **B**,[8a] palladalactam **C**,[8a] *C*,*C*-type palladacycle **D**,[8a] and palladium *a*NHC complex **E**.[8b] In this work, we demonstrate that the

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introduction of an *ortho* hydroxyl group on the *N*-phenyl ring of the ligand scaffold allow a facile preparation of novel complexes (**1** – **3**), including mononuclear and tetranuclear palladium complexes bearing tridentate *a*NHC ligands.

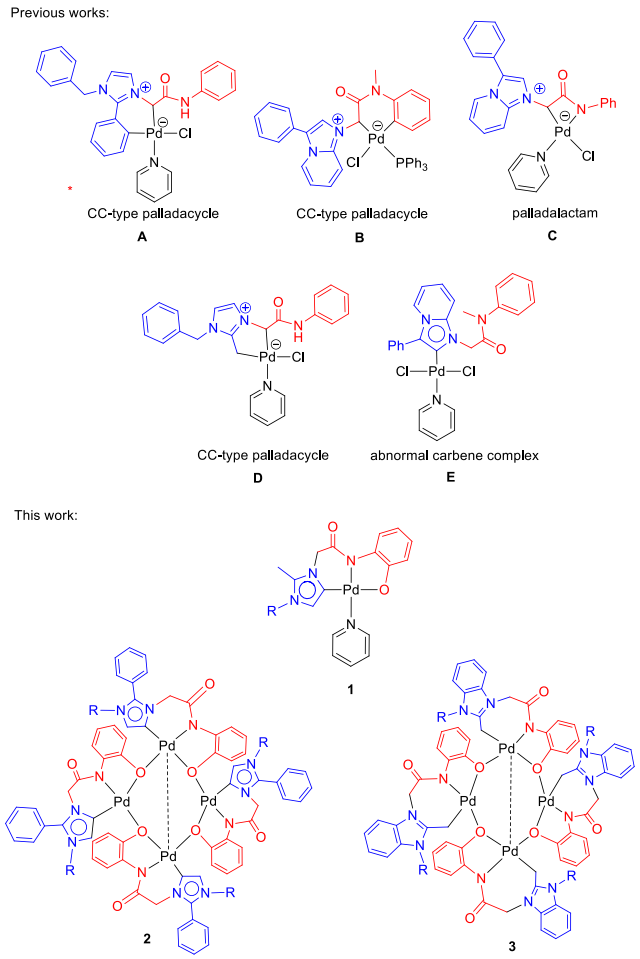

Figure 1. Palladium(II) complexes with a ligand scaffold based on an imidazolyl moiety and an amido flanking group.

The Pd-catalyzed Mizoroki-Heck coupling reaction is one of the most powerful and versatile tools currently used in synthetic organic chemistry to construct C—C bonds.[9] Among aryl halides, the use of aryl chlorides as substrates is desirable in industrial applications because they are inexpensive and widely available. However, highly effective palladium catalyst systems are needed for the activation of stronger Ar—Cl bonds. While remarkable progress has been made with the effective use of even deactivated aryl chlorides by phosphine-assisted catalyst systems,[10] it is still necessary to develop cost-effective phosphine-free catalysts with low Pd loading in green reaction media. Although mononuclear Pd–NHC complexes are shown to be highly versatile in catalyzing the reaction, [2] most of these systems suffer from poor performance of deactivated and electron-rich aryl chloride substrates. [21] Herein, we also present the catalytic activities of **1**–**3** in Mizoroki-Heck coupling reaction conducted in a molten salt. We found that the tetranuclar palladium complex with *a*NHC ligand was extremely effective with a wide range of aryl chlorides including deactivated substrates, affording quantitative yields of coupled products with a low Pd loading in most cases.

Results and Discussion

The synthesis of the two series of target ligand precursors is shown in Scheme 1. The key feature in these precursors is an *ortho* OH group on the *N*-phenyl rings; the ligands are potentially tridentate after triple deprotonation of the O*H*, N*H*(C=O), and one of the protons either on the imidazole ring or C2-methyl/phenyl groups. For ligand precursors **La–e**, the 2-position of the heterocyclic ring is blocked by a phenyl or a methyl group, preventing the possibility of normal NHC coordination. However, *a*NHC coordination is possible after deprotonation at the C5 position of the imidazole ring. For ligand precursors **Lf–g**, the imidazole ring is replaced with a benziimidazole, thus eliminating the possibilities of normal and abnormal NHC coordination. Hence, deprotonation can only occur on the C2-methyl group (see **D** in Figure 1).

Imidazolium salts **La–e** were straightforwardly obtained through the reactions of appropriate imidazole derivatives with 2-chloro-*N*-(2-hydroxyphenyl)acetamide in DMF at high temperature with modest yields in the range of 50–78%. Notably, the reactions proceeded smoothly without interference from the free hydroxy groups and thus their protection was not necessary. Ligand precursors **Lf–g** featuring a benziimidazole instead of an imidazole moiety were similarly obtained with mediocre yields of 53 and 49%, respectively. All the new non-hygroscopic white solids were characterized using NMR spectroscopy and high-resolution electron-spray mass spectrometry. Typically, two downfield broad signals were observed in their ^{1}H NMR spectra. With reference to our previous work on structurally related compounds,[11] the most downfield signal at *ca*. 10 ppm was attributed to the O*H* proton, while the second most downfield signal at ca. 9.8 ppm was attributed to the N*H* proton.

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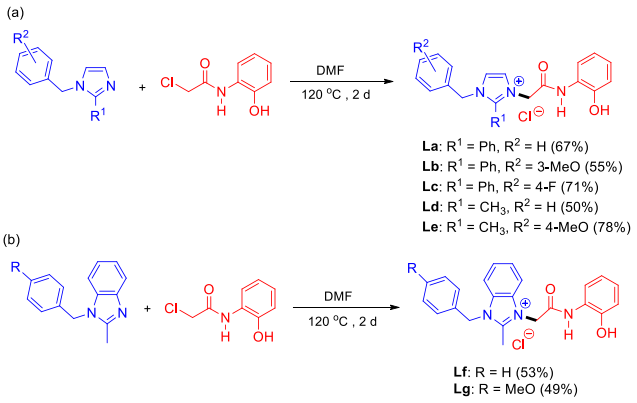
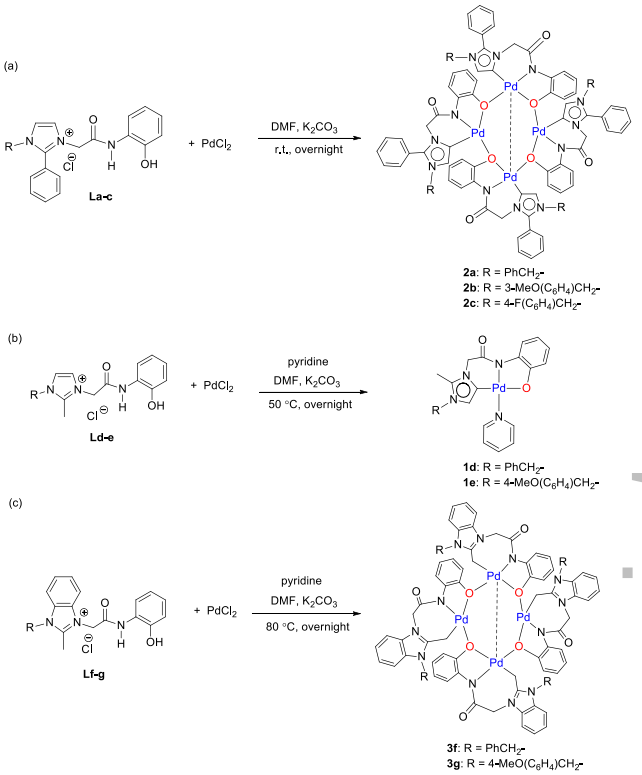


Scheme 1. Synthesis of ligand precursors.

The coordination chemistry between the new ligand precursors and palladium dichloride was thoroughly investigated. Reactions of the ligand precursors **La**–**c** featuring a C2-phenyl group with $PdCl_2$ using potassium carbonate as the base in DMF at room temperature afforded pure compounds of tetranuclear palladium complexes featuring tridentate *a*NHC ligands (Scheme 2a). The successful formation of the tetranuclear palladium complexes was unambiguously confirmed by the representative ESI-MS analysis of two of these compounds in solution and single-crystal X-ray diffraction studies (*vide infra*). For **2a**, the molecular peak of the compound was observed as the base peak at *m*/*z* = 1951.2 (theoretical *m*/*z* = 1951.2). The base peak of **2b** at *m*/*z* = 2072.3 was attributable to the $[M+H]^+$ ion (theoretical *m*/*z* = 2072.3). The characteristic abnormal carbene carbon resonances were observed at *ca*. 131 ppm, which were comparable to those of relevant palladium *a*NHC complexes.[12] Notably, the reaction between the ligand precursors and $PdCl_2$ yielded only palladium *a*NHC complexes. The C—H activation at the C2-phenyl ring, as seen in **A** (see Figure 1), was not observed. Also, the μ-phenoxide bridge in **2** was strong, as attempts to heat a solution of the tetranuclear complex with pyridine or PPh_3 did not yield any mononuclear complex such as **1d** and **1e** (*vide infra*).



Scheme 2. Synthesis of mononuclear and tetranuclear palladium complexes.

However, the reactions of ligand precursors **Ld** and **Le** bearing C2-methyl protecting groups with $PdCl_2$ under the same reaction conditions, failed to deliver the desired tetranuclear palladium *a*NHC complexes. We projected that C2-methyl substituted imidazolium compounds **Ld** and **Le** would be more electron-rich than C2-phenyl substituted compounds **La** and **Lb** and therefore hypothesized that adding pyridine as an extra organic base and conducting the complexation reactions at elevated temperature might assist deprotonation at the C5 position. Indeed, pure products of **1d** and **1e** were obtained (Scheme 2b). Subsequent characterization including single-crystal X-ray diffraction studies revealed that complexes **1d**,**e** were mononuclear palladium *a*NHC complexes. The *a*NHC ligand was chelated in a tridentate CNO fashion with pyridine occupying the fourth coordination site. Thus, in addition to acting as a base, the coordination property of pyridine also plays a crucial role in the formation of these mononuclear complexes. Noteworthy, when pyridine was added to the aforementioned preparation of complexes **La-c**, a mixture of products was obtained, presumably due to the formation of both tetranuclear and mononuclear complexes of *a*NHCs.

In the ligand precursors **Lf** and **Lg**, the possibilities of both normal and abnormal NHC coordination were eliminated. The only possible metal coordination of the third donor group was via CH_2 coordination after methyl group deprotonation. We have previously reported CH_3 activation and the formation of carbon-coordinated palladium complexes (see **D** in Figure

1).[8a] We carried out the reaction between ligand precursor **Lf** and **Lg** with $PdCl_2$ under identical reaction conditions for **2a**–**c**, however, no pure product was obtained. We next added pyridine and carried out the reaction at 80 °C with the aim of assisting deprotonation of the methyl group (Scheme 2c),[8a] tetranuclear complexes **3f** and **3g** were successfully obtained. The multinuclear nature of these tetranuclear complexes was confirmed by a crude X-ray structural analysis of **3g**. Despite the limited quality of the structural data ($R_1 > 0.1$) due to poor crystal quality, the connectivity of atoms was unambiguously confirmed (see Figure S1 in Electronic Supporting Information). The aforementioned ESI-MS analysis for **2a** and **2b** showed the molecular peaks as base peaks, indicating high stability in solution. In contrast, the ESI-MS analysis of **3f** revealed a complex spectrum with multiple signals in a wide range of *m*/*z* 700–1800 (theoretical *m*/*z* for M^+ = 1903.2), implying much lower stability in solution. Notably, a comparison of Scheme 2b vs. 2c clearly showed that *a*NHC coordination in **1d** and **1e** was more favorable than the methylene coordination as found in **3f** and **3g**. In contrast to the mononuclear **1d** and **1e**, tetranuclear complexes **3f** and **3g** were formed even when their complexation reactions were carried out in the presence of pyridine.

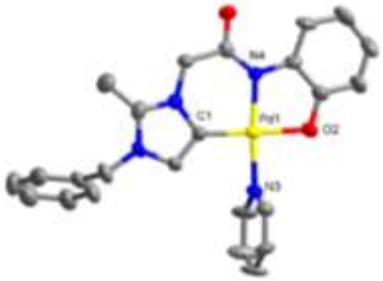


Figure 2. Molecular structure of **1d** at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1—O2, 2.016(5); Pd1—N4, 2.022(7); Pd1—C1, 1.9308(8); Pd1—N3, 2.037(7); O2—Pd1—N4, 84.9(2); C1—Pd1—N4, 94.8(3); C1—Pd1—N3, 88.9(3); O2—Pd1—N3, 91.4(2); N3—Pd1—N4, 176.3(3); C1—Pd1—O2, 179.6(3).

The structures of **1d**, **2b**, and **2c** have been successfully established in single-crystal X-ray diffraction studies. Table S1 in the Supporting Information provides the crystallographic data. The tridentate coordination of the ligand involving an *a*NHC coordination in **1d** was confirmed with the palladium center adopting a slightly distorted square-planar coordination environment (Figure 2). Generally, the most striking feature of all the new structures are the very short Pd—C bond distances. To the best of our knowledge, the Pd—C bond distance of 1.9308(8) Å in **1d** is the shortest of those reported in palladium imidazole-based *a*NHC complexes, which have Pd—C bond distance ranging from 1.951 Å[13] to 2.022 Å.[7c] The Pd—C bond distances in **2b** were even shorter (*vide infra*), while the Pd—N bond distance from pyridine N atom (2.037(7) Å) was slightly longer than from the amidate N atom (2.022(7) Å), reflecting stronger coordination from the latter donor.

The tetranuclear nature of **2b** was unambiguously established in the structural studies (Figure 3). Each palladium center in **2b** adopts distorted square planar coordination environment and is coordinated by a tridentate ligand via an abnormal carbenic C atom, amidate N atom, and μ-phenolic oxygen atom. The remaining coordination site is occupied by a bridging phenolic O atom from an adjacent ligand. The four palladium centers are not coplanar. The interatomic axis between Pd2 and Pd3 atoms is above and approximately normal to that between Pd1 and Pd4 atoms. Interestingly, Pd2 interacts weakly with Pd3 atom with a contact distance of 3.1784(7) Å (sum of van der Waals radii of Pd = 3.26 Å).[14] Such interaction is absent between Pd1 and Pd4 atoms; where the corresponding interatomic distance is ca 3.27 Å. The very short Pd—C distances involving Pd1, Pd2, and Pd3 ranged from 1.920(6)—1.928(6) Å. The corresponding distance involving Pd4 was slightly longer (1.947(7) Å).

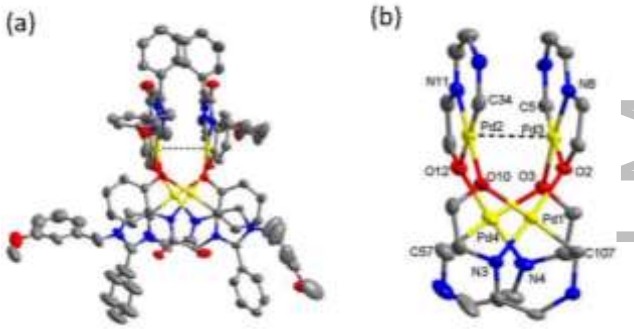


Figure 3. Molecular structure of **2b** at 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1—O2, 2.016(5); Pd1—N4, 2.022(7); Pd1—C1, 1.9308(8); Pd1—N3, 2.037(7); O2—Pd1—N4, 84.9(2); C1—Pd1—N4, 94.8(3); C1—Pd1—N3, 88.9(3); O2—Pd1—N3, 91.4(2); N3—Pd1—N4, 176.3(3); C1—Pd1—O2, 179.6(3).

Complex **2c** crystallizes in an orthorhombic space group, where the tetranuclear complex is situated on a special position along a crystallographic 2-fold axis along the *c*-axis (Figure 4). The structural features of **2c** are similar to those of **2b**. There is also a weak interaction in **2b** between a pair of Pd atoms with a contact distance of 3.1759(11) Å, comparable to that of **2c**. The interatomic distance between the other pair of Pd atoms is much larger (3.301 Å). The bond distances between the Pd atom and the *a*NHC moieties are ca. 1.932 Å.

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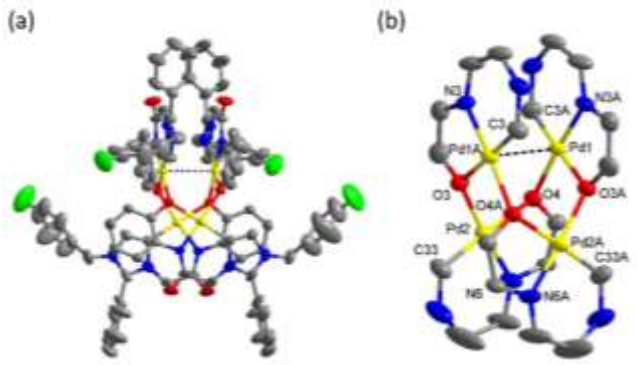
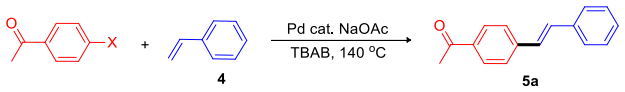


Figure 4. (a) Molecular structure of **2c** at 50 % probability level. Hydrogen atoms are omitted for clarity. (b) A simplified view of molecular structure of **2c** showing the connectivity around palladium centers. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1—O4, 2.064(5); Pd1—O3A, 2.054(5); Pd1—N3A, 1.989(6); Pd1—C3A, 1.932(8); Pd2—O3, 2.053(5); Pd2—O4, 2.060(5); Pd2—N6, 2.002(6); Pd1—C33, 1.931(8); O4—Pd1—O3A, 92.1(2); O3A—Pd1—N3A, 83.5(2); C3A—Pd1—N3A, 95.2(3); O4—Pd1—C3A, 89.2(3); O4—Pd1—N3A, 175.5(3); C3A—Pd1—O3A, 178.7(3); O3—Pd1—C33, 89.1(3); O3—Pd2—O4, 92.7(2); O4—Pd2—N6, 83.1(2); C33—Pd1—N6, 95.1(3); O3—Pd1—N6, 175.7(2); C32—Pd1—O4, 177.1(3). Nonbonding distance (Å): Pd1···Pd1A, 3.1759(11). Symmetry code: A, 0.5 – x, –y, z.

The catalytic activity of new complexes in the Mizoroki-Heck reaction was investigated (Table 1). The use of highly polar molten salts (the so-called nonaqueous ionic liquids) as green reaction media in Mizoroki-Heck reaction is believed to facilitate cationic mechanism in the reaction and stabilize underligated Pd(0) species by forming anionic complexes with halide ions,[9c,15] leading to enhanced PhCl reactivity.[9c,15a,16] We previously conducted successful Mizoroki-Heck reactions in molten *n*-tetrabutylammonium bromide (TBAB).[12a,17] To screen for the most efficient complex, a benchmark reaction between 4-chloroacetophenone and styrene (**4**) using 0.2 mol% of Pd atom loading (i.e., 0.05 mol% of a tetranuclear complex) was carried out using our reported reaction conditions (NaOAc as base, molten TBAB as solvent, 140 °C, 2 h).[17f] Of the new complexes (entries 1−7), both mononuclear *a*NHC complex **1d** and tetranuclear *a*NHC complex **2b** afforded quantitative yields of product (entries 1 and 4). Reducing the Pd atom loading to 0.1 mol% revealed that tetranuclear complex **2b** was more effective than mononuclear complex **1d**, resulting in an improved 54 % product yield (entries 8 vs 9). Using H_2O/NMP as a solvent and K_2CO_3 as a base as reported by Knölker *et al*,[4e] the catalytic reaction was totally inhibited (entry 10). As expected, the use of more reactive bromide substrate produced higher TONs and TOFs (entries 11−13). A small 0.05 mol% Pd loading of complex **2b** was sufficient for delivering a good TOF of 470 h^{-1} (entry 12). This is comparable to the TOF of 427 h^{-1} of the tetranuclear palladium complex that was reported by Knölker et al. for the same reaction.[4e]

Table 1. Mizoroki-Heck reaction of 4-chloroacetophenone with styrene [a)]



Entry	Complex	mol % Pd atom	X	Time	Yield (%)	TON	TOF
1	**1d**	0.2	Cl	2	100 (96:4)	500	250
2	**1e**	0.2	Cl	2	65 (97:3)	325	163
3	**2a**	0.2	Cl	2	64 (97:3)	320	160
4	**2b**	0.2	Cl	2	100 (96:4)	500	250
5	**2c**	0.2	Cl	2	86 (97:3)	430	215
6	**3f**	0.2	Cl	2	85 (96:4)	425	213
7	**3g**	0.2	Cl	2	83 (96:4)	415	208
8	**1d**	0.1	Cl	2	17	170	85
9	**2b**	0.1	Cl	2	54 (97:3)	540	270
10	**2b**	0.2	Cl	4	0 [b)]	--	--
11	**2b**	0.1	Br	2	84	840	420
12	**2b**	0.05	Br	4	94 (96:4)	1880	470
13	**2b**	0.02	Br	4	18	900	225

[a)] Reaction conditions: 1.4 mmol of styrene, 1 mmol of aryl halide, 1.1 mmol of NaOAc, 2 g of TBAB, Pd cat., 140 °C. Yield determined by NMR using 1,3,5-trimethoxybenzene as internal standard, anti/gem ratio in parenthesis. [b)] H_2O/NMP, K_2CO_3, 100 °C.

After the most efficient tetranuclear complex **2b** was identified, the substrate scope of the catalyst system was investigated (Table 2). The complex proved to be highly efficient for the coupling reaction of activated aryl chlorides such as 4-chloronitrobenzne, 4-chlorocyanobenzene, 1-chloro-4-(trifluoromethyl)benzene, 4-chlorobenzaldehyde, and 4-chloroacetophenone with styrene, producing quantitative yields of the corresponding coupled products in 2 − 6 h (entries 1 − 5). Increasing the reaction time to 12 h, complex **2b** was also highly effective for the utilization of electron-neutral substrates such as chlorobenzene and 4-chlorotoluene, affording quantitative yields (entries 6 and 7). A quantitative product yield was also achieved with the unreactive electron-rich 4-chloroanisole (entry 8).

Next, we tested the viability of the catalyst system for handling sterically hindered substrates. The system proved highly effective, producing quantitative yields with slightly hindered *meta*-substituted aryl chlorides (entries 9, 11, 12, and 13). Notably, entry 13 represents the first time that 1-chloro-3,5-dimethoxybenzene can be applied as a substrate in the Mizoroki-Heck coupling reaction with styrene. In previous reports, more reactive alkene partners than simple styrene, such as 1-

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alkenyltrifluoroborate[18] or 1-alkenylboronic acid,[19] were required for the formation of **5hh** when using the deactivated aryl chloride as a substrate. However, compared with examples in the literature,[10c,16] the catalyst system was less effective at handling *ortho*-substituted aryl chlorides; the use of 2-chlorobenzonitrile produced only a poor 36% yield of coupled product with styrene (entry 10).

Even though there are two possible sites for C–C bond formation when 1,4-dichlorobenzene was used as substrate, the reaction was highly selective, producing only the mono-alkene product (entry 14). Double Heck coupling was not observed even if styrene was in excess. The quantitative yield of **5i** is the highest among reports of the same catalytic reaction.[20]

The substrate scope was then examined with respect to the alkenes partners. Entry 15 shows that 4-chloroacetophenone can react with 4-chlorostyene with a quantitative product yield within 2 h. However, when a slightly electron-rich 4-methystyrene was used, a longer reaction time of 6 h was required (entry 16). When aryl chloride substrates with electron-donating substituents were used (entries 17 and 18), an even longer reaction time of 12 h was required. The quantitative production of coupled product **7g** in entry 17 represents the best reported yield of the same coupling reaction.[21] For the coupling reaction between 4-chloroanisole and 4-methystyrene, only one paper reported satisfactory yields of coupled product (62–70%), with a higher 1 mol% Pd loading and a prolonged reaction time of 44 h.[21b] In contrast, our catalyst system was much more effective, delivering a quantitative yield of **7h** with a mild 0.2 mol% Pd loading in 12 h (entry 18). Entries 19–20 show that 4-methoxystyrene can also be smoothly applied to reactions with electron-rich and electron-neutral aryl chlorides. However, in reactions with deactivated 4-chloroanisole, a poor 40% yield of coupled product **8h** was obtained (entry 21). The only existing paper on the coupling reaction between 4-chloroanisole and 4-methoxystyrene reported that the compound **8h** had a good 83% yield; however, a higher Pd loading of 1 mol% was required.[22] We repeated the reaction with a 1 mol% of Pd loading and a comparable 79% of product yield was obtained.

Table 2. Mizoroki-Heck coupling reaction of aryl chlorides catalyzed by tetranuclear complex **2b** [a)]

Entry	Ar—X	Product	Time (h)	Yield (%)

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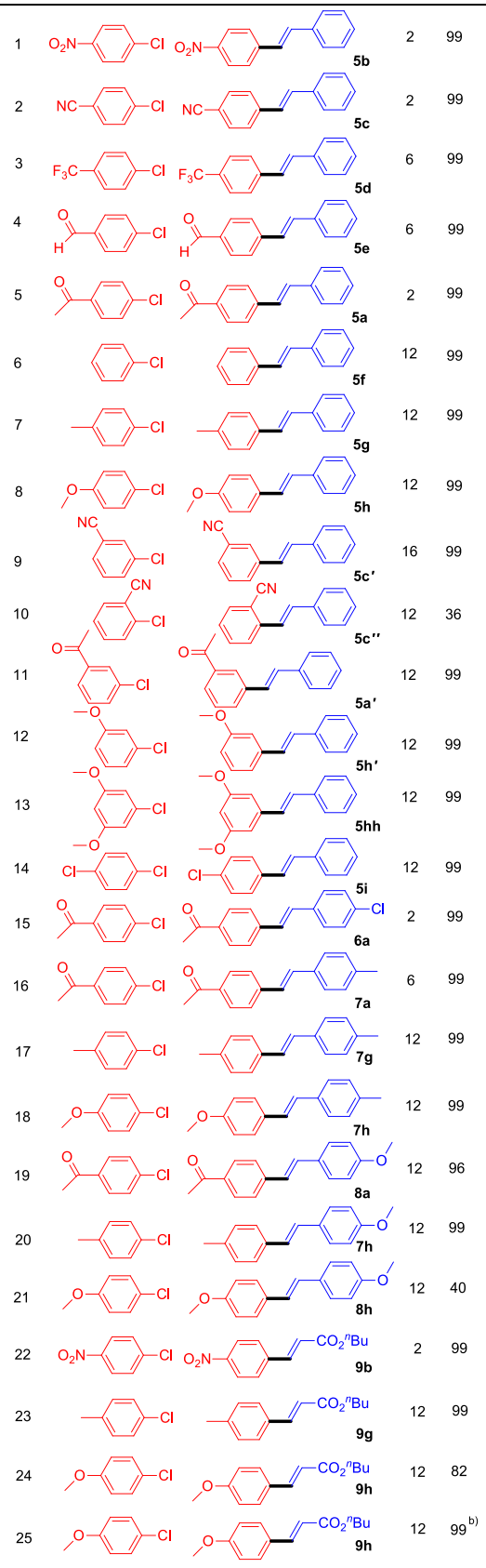
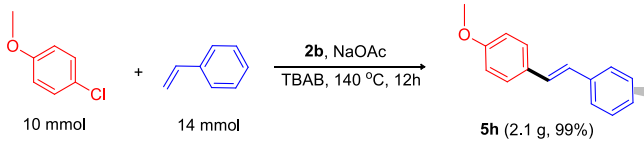


[a] Reaction conditions: 1.4 mmol of styrene, 1 mmol of aryl halide, 1.1 mmol of NaOAc, 2 g of TBAB, 0.05 mol% **2b** (i.e. 0.2 mol% of Pd atom loading), 140 °C. Isolated yield. [b] Methyl acrylate was used as the alkene coupling partner.

Also, *n*-butyl acrylate was successfully employed as a substrate, resulting in quantitative yields of products with electron-rich and electron-neutral aryl chlorides (entries 22 and 23). However, a slightly lower yield of 82% was obtained with 4-chloroanisole (entry 24). Interestingly, when methyl acrylate was used as a substrate, a tandem Heck/transesterification reaction occurred, producing a quantitative yield of the coupled product **9h** (entry 25). The transesterification involving the TBAB solvent was previously observed by us.[17f]



Scheme 3. The Mizoroki-Heck reaction of 4-chloroanisole and styrene in a preparative scale.

Finally, to demonstrate the utility of the catalyst system based on **2b** in synthetic organic chemistry, we conducted a reaction between deactivated 4-chloroanisole (10 mmol) and styrene (14 mmol) in a preparative scale, which successfully resulted in a quantitative yield of 2.1 g of the coupled product **5h** (Scheme 3).

Conclusion

We designed and prepared two novel series of ligand precursors with an *ortho* hydroxy group incorporated on the *N*-phenyl ring of the ligand scaffold based on an imidazolyl/benziimidazoly moiety and a *N*-$CH_2C(=O)NR'Ph$ side-arm. This structural fine tuning of the ligand scaffold allowed for the synthesis of tetranuclear palladium complexes including the first example of such multinuclear complexes with *a*NHC ligands. As evidenced from the extremely short Pd─C bond distances in representative crystal structures, the electron-donating *a*NHC moiety bind strongly to the palladium centers in both the mononuclear and tetranuclear complexes. The extremely effective catalytic activities of the tetranuclear palladium *a*NHC complexes in the Mizoroki-Heck coupling reaction seem to correlate well with their short Pd─carbene bond distances. The robust tetranuclear complex **2b** was capable of using a wide range of aryl chlorides including unreactive deactivated substrates; in many examples, quantitative yields of coupled products were obtained. Interestingly, the catalytic activity of the tetranuclear complex is superior to that of its mononuclear counterpart. The rate-determining step of the reaction is believed to be the oxidative addition of aryl chlorides. The highly effective catalytic activity of the tetranuclear *a*NHC complex **2b** may be related to a higher local concentration of active electron-rich LPd(0) which favors the oxidative addition of the

unreactive C—Cl bonds. The molten TBAB solvent may stabilize the active species, contributing also to the enhanced activity of aryl chlorides.

Experimental Section

General Information

All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with standard procedures. Starting chemicals were purchased from commercial source and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 and 75.47 MHz, respectively, on a Bruker AV-300 spectrometer. Elemental analyses were performed on a Thermo Flash 2000 CHN-O elemental analyzer. ESI-MS was carried out on a Finnigan/Thermo Quest MAT 95XL mass spectrometer at National Chung Hsing University (Taiwan).

Synthesis of 1-Benzyl-3-(2-((2-hydroxyphenyl)amino)-2-oxoethyl)-2-phenyl-1*H*-imidazol-3-ium Chloride (La)

A mixture of 1-benzyl-2-phenyl-*1H*-imidazole (1.01 g, 4.31 mmol) and (0.80 g, 4.31 mmol) in DMF (20 mL) was placed in a Schlenk flask. The mixture was heated to 120 ^{o}C overnight. After cooling, the white solid was collected on a frit, washed with THF, and dried under vacuum. Yield: 1.2 g (67 %). M.p. = 246.1–246.5 °C; ^{1}H NMR ([D$_6$]DMSO): δ 5.14 (s, 2H, C*H*$_2$), 5.35 (s, 2H, C*H*$_2$), 6.71 (t, ^{3}*J*(HH) = 6.0 Hz, 1H, Ar *H*), 6.92 (t, ^{3}*J*(HH) = 6.0 Hz, 1H, Ar *H*), 7.00–7.07 (m, 3H, Ar *H*), 7.30 (s, 3H, imi *H*, Ar *H*), 7.60–7.70 (m, 6H, Ar *H*), 8.15 (d, ^{3}*J*(HH) = 9.0 Hz, 2H, Ar *H*), 9.90 (s, 1H, N*H*), 10.26 ppm (s, 1H, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ=51.5 (*C*H$_2$), 51.9 (*C*H$_2$), 116.1, 119.1, 121.3 (quaternary *C*), 122.8, 122.9, 124.7, 125.5, 125.6 (quaternary *C*), 127.9, 128.9, 129.3, 130.0, 130.9, 133.1, 134.9 (quaternary *C*), 145.7 (quaternary *C*), 148.8 (quaternary *C*), 164.2 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{24}H_{22}N_3O_2$ [M–Cl]$^{+}$ 384.1711; found 384.1706.

Synthesis of 3-(2-((2-Hydroxyphenyl)amino)-2-oxoethyl)-1-(3-methoxybenzyl)-2-phenyl-1*H*-imidazol-3-ium Chloride (Lb)

The compound was prepared with a similar procedure to that of **La**. A mixture of 1-(3-methoxybenzyl)-2-phenyl-1*H*-imidazole (1.1 g, 4.16 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (0.77 g, 4.16 mmol) was used. A white solid was obtained. Yield: 1.0 g (55 %); M.p. = 195.1–195.8 °C; ^{1}H NMR ([D$_6$]DMSO): δ 3.67 (s, 3H, OC*H*$_3$), 5.13 (s, 2H, C*H*$_2$), 5.31 (s, 2H, C*H*$_2$), 6.61–6.73 (m, 3H, Ar *H*), 6.86–7.01 (m, 3H, Ar *H*), 7.23 (t, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 7.61–7.69 (m, 6H, imi *H*, Ar *H*), 8.13 (d, ^{3}*J*(HH) = 15.0 Hz, 2H, Ar *H*), 9.87 (s, 1H, N*H*), 10.21 ppm (s, 1H, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 51.5 (*C*H$_2$), 51.8 (*C*H$_2$), 55.6 (OC*H*$_3$), 113.6, 114.4, 116.1, 119.1, 119.9, 121.3 (quatenary *C*), 122.8, 122.9, 124.7, 125.6, 130.0, 130.5, 130.9, 133.1, 136.4 (quatenary *C*), 145.7 (quatenary *C*), 148.8 (quatenary *C*), 159.9 (quatenary *C*), 164.2 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{25}H_{24}N_3O_3$ [M–Cl]$^{+}$ 414.1817; found 414.1821.

Synthesis of 1-(4-Fluorobenzyl)-3-(2-((2-hydroxyphenyl)amino)-2-oxoethyl)-2-phenyl-1*H*-imidazol-3-ium Chloride (Lc)

The compound was prepared with a similar procedure to that of **La**. A mixture of 1-(4-fluorobenzyl)-2-phenyl-1*H*-imidazole (1.0 g, 3.96 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (0.74 g, 3.96 mmol) was used. A white solid was obtained. Yield: 1.1 g (71 %). M.p. = 114.2–114.6 °C; ^{1}H NMR ([D$_6$]DMSO): δ 5.08 (s, 2H, C*H*$_2$), 5.32 (s, 2H, C*H*$_2$), 6.73 (t, ^{3}*J*(HH) = 6.0 Hz, 1H, Ar *H*), 6.92 (s, 2H, imi *H*), 7.12–7.21 (m, 5H, Ar *H*), 7.57–7.74 (m, 5H, Ar *H*), 8.06 (d, ^{3}*J*(HH) = 3.0 Hz, 2H, Ar *H*), 9.75 (s, 1H, N*H*), 10.08 ppm (s, 1H, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 51.2 (*C*H$_2$), 51.4 (*C*H$_2$), 116.1, 116.2 (d, ^{2}*J*(CF) = 21.9 Hz, Ar *C*), 119.1, 121.3 (quaternary *C*), 122.9, 124.6, 125.5, 130.0, 130.4 (d, ^{3}*J*(CF) = 8.3 Hz, Ar *C*), 130.9, 131.0 (quaternary *C*), 131.1 (quaternary *C*), 133.1, 145.6 (quaternary *C*), 148.8 (quaternary *C*), 162.4 (d, ^{1}*J*(CF) = 245.3 Hz, *C*F), 164.1 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{24}H_{21}FN_3O_2$ [M–Cl]$^{+}$ 402.1617; found 402.1605.

Synthesis of 1-Benzyl-3-(2-((2-hydroxyphenyl)amino)-2-oxoethyl)-2-methyl-1*H*-imidazol-3-ium Chloride (Ld)

The compound was prepared with a similar procedure to that of **La**. A mixture of 1-benzyl-2-methyl-*1H*-imidazole (1.41 g, 8.19 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (1.52 g, 8.19 mmol) in DMF (20 mL) was used. A white solid was obtained. Yield: 1.46 g (50 %). M.p. = 250.6–251.2 °C; ^{1}H NMR ([D$_6$]DMSO): δ 2.59 (s, 3H, C*H*$_3$), 5.27 (s, 2H, C*H*$_2$), 5.49 (s, 2H, C*H*$_2$), 6.74 (t, 1H, ^{3}*J*(HH) = 6.0 Hz, Ar *H*), 6.94 (s, 2H, imi *H*), 7.31−7.46 (m, 5H, Ar *H*), 7.79 (d, 3H, ^{3}*J*(HH) = 9.0 Hz, Ar *H*), 9.98 ppm (*br* s, 2H, N*H*, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 10.2 (*C*H$_3$), 51.0 (*C*H$_2$), 51.1 (*C*H$_2$), 116.1, 119.2, 121.9, 122.9, 123.5, 125.6, 125.7 (quaternary *C*), 128.1, 129.0, 129.5, 135.0 (quaternary *C*), 146.2 (quaternary *C*), 148.8 (quaternary *C*), 164.1 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{19}H_{20}N_3O_2$ [M–Cl]$^{+}$ 322.1555; found 322.1557.

Synthesis of 3-(2-((2-Hydroxyphenyl)amino)-2-oxoethyl)-1-(4-methoxybenzyl)-2-methyl-1*H*-imidazol-3-ium Chloride (Le)

The compound was prepared with a similar procedure to that of **La**. A mixture of 1-(4-methoxybenzyl)-2-methyl-*1H*-imidazole (0.91 g, 4.50 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (0.84 g, 4.50 mmol) was used. A white solid was obtained. Yield: 1.37 g (78 %). M.p. = 223.8–224.2 °C; ^{1}H NMR ([D$_6$]DMSO): δ 2.61 (s, 3H, C*H*$_3$), 3.74 (s, 3H, OC*H*$_3$), 5.29 (s, 2H, C*H*$_2$), 5.41 (s, 2H, C*H*$_2$), 6.73 (t, 1H, ^{3}*J*(HH) = 6.0 Hz, Ar *H*), 6.91–6.98 (m, 4H, Ar *H*, imi *H*), 7.33 (d, 2H, ^{3}*J*(HH) = 9.0 Hz, Ar *H*), 7.77–7.79 (m, 3H, Ar *H*), 10.0 (s, 1H, N*H*), 10.2 ppm (s, 1H, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 10.2 (*C*H$_3$), 50.7 (*C*H$_2$), 50.9 (*C*H$_2$), 55.7 (OC*H*$_3$), 114.8, 116.1, 119.2, 121.6, 122.7, 123.4, 125.5, 125.8 (quaternary *C*), 126.8 (quaternary *C*), 130.0, 145.9 (quaternary *C*), 148.7 (quaternary *C*), 159.8 (quaternary *C*), 164.0 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{20}H_{22}N_3O_3$ [M–Cl]$^{+}$ 352.1661; found 352.1659.

Synthesis of 1-Benzyl-3-(2-((2-hydroxyphenyl)amino)-2-oxoethyl)-2-methyl-1*H*-benzo[*d*]imidazol-3-ium Chloride (Lf)

The compound was prepared with a similar procedure to that of **La**. A mixture of 1-benzyl-2-methyl-*1H*-benzo[*d*]imidazole (1.1 g, 4.94 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (0.92 g, 4.94 mmol) was used. A white solid was obtained. Yield: 0.97 g (53 %). M.p. 248.5–249.1 °C; ^{1}H NMR ([D$_6$]DMSO): δ 2.98 (s, 3H, C*H*$_3$), 5.69 (s, 2H, C*H*$_2$), 5.90 (s, 2H, C*H*$_2$), 6.72–6.75 (m, 1H, Ar *H*), 6.97 (d, ^{3}*J*(HH) = 3.0 Hz, Ar *H*), 7.32–7.40 (m, 5H, Ar *H*), 7.64 (t, ^{3}*J*(HH) = 6.0 Hz, 2H, Ar *H*), 7.82 (d, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 7.98 (d, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 8.04 (d, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 10.09 (s, 1H, N*H*), 10.20 ppm (s, 1H, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 11.5 (*C*H$_3$), 48.3 (*C*H$_2$), 48.6 (*C*H$_2$), 113.4, 113.8, 116.1, 119.2, 122.6, 125.6, 125.8 (quaternary *C*), 126.9, 127.0, 127.7, 128.9, 129.5, 131.1 (quaternary *C*), 131.9 (quaternary *C*), 134.6 (quaternary *C*), 148.6 (quaternary *C*), 153.8 (quaternary *C*), 164.0 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{23}H_{22}N_3O_2$ [M–Cl]$^{+}$ 372.1711; found 372.1701.

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Synthesis of 3-(2-((2-Hydroxyphenyl)amino)-2-oxoethyl)-1-(4-methoxybenzyl)-2-methyl-1*H*-benzo[*d*]imidazol-3-ium Chloride (Lg)

The compound was prepared with a similar procedure to that of **La**. A mixture of 1-(4-methoxybenzyl)-2-methyl-*1H*-benzo[*d*]imidazole (1.0 g, 4.16 mmol) and 2-chloro-*N*-(2-hydroxyphenyl)acetamide (0.77 g, 4.16 mmol) was used. A white solid was obtained. Yield: 0.89 g (49 %). M.p. 238.4–239.2 °C; ^{1}H NMR ([D$_6$]DMSO): δ 2.98 (s, 3H, C*H*$_3$), 3.73 (s, 3H, OC*H*$_3$), 5.66 (s, 2H, C*H*$_2$), 5.80 (s, 2H, C*H*$_2$), 6.70–6.76 (m, 1H, Ar *H*), 6.94–6.96 (m, 4H, Ar *H*), 7.32 (d, ^{3}*J*(HH) = 6.0 Hz, 2H, Ar *H*), 7.60–7.65 (m, 2H, Ar *H*), 7.82 (d, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 8.01 (d, ^{3}*J*(HH) = 9.0 Hz, 2H, Ar *H*), 10.04 (s, 1H, N*H*), 10.10 ppm (s, 1H, O*H*); ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 11.5 (*C*H$_3$), 48.2 (*C*H$_2$), 55.7 (OCH$_3$), 113.3, 113.9, 114.9, 116.1, 119.2, 122.5, 125.6, 125.8 (quaternary *C*), 126.5 (quaternary *C*), 126.8, 127.0, 129.5, 131.0 (quaternary *C*), 131.9 (quaternary *C*), 148.6 (quaternary *C*), 153.6 (quaternary *C*), 159.7 (quaternary *C*), 164.0 ppm (*C*=O); HRMS (ESI) *m/z* calcd for $C_{24}H_{24}N_3O_3$ [M–Cl]$^+$ 402.1817; found 402.1808.

Synthesis of [1-Benzyl-2-methyl-3-[2-oxo-2-[(2-phenolato-κ*O*)amino-κ*N*]ethyl]-1*H*-imidazoliumato-κ*C*^{4}](pyridine)palladium (1d)

To a 20 mL Schlenk flask, $PdCl_2$ (0.050 g, 0.28 mmol), **Ld** (0.1 g, 0.28 mmol), pyridine (22.6 µL, 0.28 mmol), and K_2CO_3 (0.15 g, 1.1 mmol) were dissolved in dry DMF (10 mL) under nitrogen atmosphere. The solution was allowed to stir at 50 ºC overnight. The residual was extracted with DCM/H_2O twice. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a solid. Diethyl ether was added and the yellowish solid formed was collected on frit and dried under vacuum. Yield: 0.12 g (85 %). M.p. 225.1–225.4 °C (dec.); ^{1}H NMR ([D$_6$]DMSO): δ 2.59 (s, 3H, C*H*$_3$), 4.70 (s, 2H, C*H*$_2$), 5.34 (s, 2H, C*H*$_2$), 6.19–6.40 (m, 2H, Ar *H*), 6.56 (t, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 7.10 (s, 1H, imi *H*), 7.23–7.39 (m, 4H, py *H*, Ar *H*), 7.53–7.66 (m, 2H, Ar *H*), 7.79 (t, ^{3}*J*(HH) = 9.0 Hz, 1H, py *H*), 8.00–8.18 (m, 2H, Ar *H*), 8.77 ppm (d, ^{3}*J*(HH) = 6.0 Hz, 2H, py *H*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 14.5 (*C*H$_3$), 50.9 (two overlapping *C*H$_2$), 120.1, 120.3 (quaternary *C*), 124.8 (py *C*), 127.2, 128.5, 128.6, 129.3, 129.9 (quaternary *C*), 130.8 (Pd — *C*), 134.3 (quaternary *C*), 138.4 (py *C*), 146.1 (quaternary *C*), 153.2 (Py *C*), 163.1 ppm (*C*=O); Elemental analysis calcd (%) for $C_{24}H_{22}N_4O_2Pd$: C, 57.13; H, 4.39; N, 11.11; found: C, 57.47; H, 4.59; N, 10.94 %.

Synthesis of [1-[(4-Methoxyphenyl)methyl]-2-methyl-3-[2-oxo-2-[(2-phenolato-κ*O*)amino-κ*N*]ethyl]-1*H*-imidazoliumato-κ*C*^{4}](pyridine)palladium (1e)

The complex was prepared with a similar procedure to that of **1d**. A mixture of $PdCl_2$ (0.046 g, 0.26 mmol), **Le** (0.10 g, 0.26 mmol), pyridine (20.9 µL, 0.26 mmol), and K_2CO_3 (0.14 g, 1.0 mmol) was used. A yellow solid was obtained. Yield: 0.095 g (69 %). M.p. 226.9–227.1 °C (dec.); ^{1}H NMR (CDCl$_3$): δ 2.19 (s, 3H, C*H*$_3$), 3.74 (s, 3H, OC*H*$_3$), 4.57 (s, 2H, C*H*$_2$), 4.97 (s, 2H, C*H*$_2$), 6.40 (t, ^{3}*J*(HH) = 9.0 Hz, 1H, Ar *H*), 6.68–6.85 (m, 7H, imi *H*, py *H*, Ar *H*), 7.41 (t, ^{3}*J*(HH) = 6.0 Hz, 2H, Ar *H*), 7.80 (t, ^{3}*J*(HH) = 9.0 Hz, 1H, py *H*), 8.24 (d, ^{3}*J*(HH) = 6.0 Hz, 1H, Ar *H*), 8.97 ppm (d, ^{3}*J*(HH) = 6.0 Hz, 2H, py *H*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ=10.1 (*C*H$_3$), 50.6 (*C*H$_2$), 55.4 (OCH$_3$), 56.1 (*C*H$_2$), 113.5, 114.5, 116.3, 121.4, 123.1, 123.5, 125.4 (py *C*), 125.9 (quaternary *C*), 128.3, 129.9 (quaternary *C*), 131.6 (Pd—*C*), 137.9 (Py *C*), 145.1 (quaternary *C*), 149.9 (quaternary *C*), 153.1 (py *C*), 159.7 (quaternary *C*), 164.2 ppm (*C*=O); elemental analysis calcd (%) for $C_{25}H_{24}N_4O_3Pd$: C, 56.17; H, 4.52; N, 10.48; found: C, 56.48; H, 4.97; N, 10.66 %.

Synthesis of Tetrakis[μ-1-benzyl-2-phenyl-3-[2-oxo-2-[(2-phenolato-κ*O*)amino-κ*N*]ethyl]-1*H*-imidazoliumato-κ*C*^{4}]tetrapalladium (2a)

To a 20 mL Schlenk flask, $PdCl_2$ (0.042 g, 0.28 mmol), **La** (0.1 g, 0.24 mmol) and K_2CO_3 (0.13 g, 0.96 mmol) were dissolved in dry DMF (10 mL) under nitrogen atmosphere. The solution was allowed to stir at room temperature. The residual was extracted with DCM/H_2O twice. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a yellow solid, which was washed with diethyl ether and dried under vacuum. Yield: 0.092 g (79 %). M.p. 251.9–252.3 °C (dec.); ^{1}H NMR (CDCl$_3$): δ 4.46–4.67 (m, 16H, C*H*$_2$), 6.14 (s, 4H, imi *H*), 6.37 (t, ^{3}*J*(HH) = 6.0 Hz, 4H, Ar *H*), 6.65–6.98 (m, 16H, Ar *H*), 7.17–7.51 (m, 28H, Ar *H*), 7.86 (d, ^{3}*J*(HH) = 9.0 Hz, 4H. Ar *H*), 8.48 ppm (d, ^{3}*J*(HH) = 9.0 Hz, 4H, Ar *H*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 51.2 (*C*H$_2$), 55.7 (*C*H$_2$), 115.4, 120.6 (quaternary *C*), 122.6, 123.9, 127.0 (quaternary *C*), 127.2, 128.1, 128.5, 128.8, 129.1, 129.4, 129.8, 129.9, 130.3, 130.6, 130.8, 131.3 (Pd—*C*), 134.8, 135.1, 135.2, 139.9 (quaternary *C*), 142.4 (quaternary *C*), 161.5 (quaternary *C*), 165.1 ppm (*C*=O); Elemental analysis calcd (%) for $C_{96}H_{76}N_{12}O_8Pd_4$: C, 59.13; H, 3.93; N, 8.62; found: C, 59.01; H, 3.89; N, 8.43 %.

Synthesis of Tetrakis[μ-1-[(3-methoxyphenyl)methyl]-2-phenyl-3-[2-oxo-2-[(2-phenolato-κ*O*)amino-κ*N*]ethyl]-1*H*-imidazoliumato-κ*C*^{4}]tetrapalladium (2b)

The complex was prepared with a similar procedure to that of **2a**. A mixture of $PdCl_2$ (0.039 g, 0.22 mmol), **Lb** (0.10 g, 0.22 mmol) and K_2CO_3 (0.11 g, 0.88 mmol) was used. A yellow solid was obtained. Yield: 0.096 g (84 %). M.p. 269.4–270.1 °C (dec.); ^{1}H NMR (CDCl$_3$): δ 3.62 (s, 12H, C*H*$_3$), 4.47–4.70 (m, 16H, C*H*$_2$), 6.15 (s, 4H, imi *H*), 6.31–6.40 (m, 16H, Ar *H*), 6.65–6.72 (m, 8H, Ar *H*), 7.08 (t, ^{3}*J*(HH) = 9.0 Hz, 4H, Ar *H*), 7.51 (*br* s, 16H, Ar *H*), 7.87 (d, ^{3}*J*(HH) = 9.0 Hz, 4H, Ar *H*), 8.51 ppm (d, ^{3}*J*(HH) = 9.0 Hz, 4H, Ar *H*); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 51.1 (*C*H$_2$), 55.2 (*C*H$_3$), 55.7 (*C*H$_2$), 112.3, 114.0, 115.4, 119.3, 120.6 (quaternary *C*), 121.9, 122.6, 123.9, 129.4, 129.7, 129.9, 130.4, 131.3 (Pd−*C*), 136.3 (quaternary *C*), 139.9 (quaternary *C*), 142.5 (quaternary *C*), 159.8 (quaternary *C*), 161.4 (quaternary *C*), 165.1 ppm (*C*=O); Elemental analysis calcd (%) for $C_{100}H_{84}N_{12}O_{12}Pd_4$: C, 58.02; H, 4.09; N, 8.12; found: C, 58.10; H, 3.60; N, 8.05 %.

Synthesis of Tetrakis[μ-1-[(4-fluorophenyl)methyl]-2-phenyl-3-[2-oxo-2-[(2-phenolato-κ*O*)amino-κ*N*]ethyl]-1*H*-imidazoliumato-κ*C*^{4}]tetrapalladium (2c)

The complex was prepared with a similar procedure to that of **2a**. A mixture of $PdCl_2$ (0.044 g, 0.25 mmol), **Lc** (0.10 g, 0.25 mmol) and K_2CO_3 (0.14 g, 1.0 mmol) was used. A yellow solid was obtained. Yield: 0.063 g (50 %). M.p. 239.5–240.2 °C (dec.); ^{1}H NMR (CDCl$_3$): δ 4.47–4.65 (m, 16H, C*H*$_2$), 6.10 (s, 4H, imi *H*), 6.38 (t, ^{3}*J*(HH) = 6.0 Hz, 4H, Ar *H*), 6.65–6.96 (m, 24H, Ar *H*), 7.53 (*br* s, 16H, Ar *H*), 7.85 (d, ^{3}*J*(HH) = 9.0 Hz, 4H, Ar *H*), 8.46 ppm (d, ^{3}*J*(HH) = 6.0 Hz, 4H, Ar *H*); ^{13}C{^{1}H} NMR (DMSO-d_6): δ 50.0 (*C*H$_2$), 55.5 (*C*H$_2$), 115.9 (d, ^{2}*J*(CF) = 20.4 Hz, Ar *C*), 120.3, 121.1, 121.9, 122.4 (quaternary *C*), 124.1, 129.2, 129.9 (d, ^{3}*J*(CF) = 7.5 Hz, Ar *C*), 130.1, 130.8, 131.0, 131.7 (quaternary *C*), 131.9 (Pd—*C*), 140.1 (quaternary *C*), 142.6 (quaternary *C*), 161.2 (quaternary *C*), 162.1 (d, ^{1}*J*(CF) = 243.0 Hz, *C*F), 164.8 ppm (*C*=O); elemental analysis calcd (%) for $C_{96}H_{72}F_4N_{12}O_8Pd_4$: C, 57.02; H, 3.59; N, 8.31; found: C, 57.31; H, 3.87; N, 7.96 %

Synthesis of Tetrakis[μ-2-[2-(3-benzyl-2-methanidyl-κ*C*-benzimidazolium-1-yl)acetyl]azanidyl-κ*N*-phenolato-κ*O*]tetrapalladium (3f)

To a 20 mL Schlenk flask, $PdCl_2$ (0.050 g, 0.27 mmol), **Lf** (0.15 g, 0.40 mmol), pyridine (21.6 µL, 0.27 mmol), and K_2CO_3 (0.22 g, 1.61 mmol) were dissolved in dry DMF (10 mL) under nitrogen atmosphere. The solution was allowed to stir at 80 ºC overnight. The residual was extracted with DCM/H_2O twice. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness under vacuum to give a solid. MeOH was added and the orange

solid formed was collected on frit and dried under vacuum. Yield: 0.061 g (48 %). M.p. = 245.2–245.5 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.98–2.02 (m, 4H, PdC*H*aHb), 2.20–2.24 (m, 4H, PdCHa*H*b), 4.62 (s, 8H, CH_2), 4.93 (d, ^2J(HH) = 15.0 Hz, 4H, C*H*aHb), 5.20 (d, ^2J(HH) = 18.0 Hz, 4H, CHa*H*b), 6.46–6.49 (m, 8H, Ar *H*), 6.98 (*br* s, 8H, Ar *H*), 7.14-7.20 (m, 12H, Ar *H*), 7.31–7.36 (m, 8H, Ar *H*), 7.60 (d, ^3J(HH) = 9.0 Hz, 4H, Ar *H*), 8.00 (d, ^3J(HH) = 6.0 Hz, 4H, Ar *H*), 8.13 ppm (d, ^3J(HH) = 6.0 Hz, 4H, Ar *H*). ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ 6.2 (Pd*C*H$_2$), 47.4 (*C*H$_2$), 50.7 (*C*H$_2$), 111.7, 112.3, 113.0, 115.9, 122.3, 123.6, 125.4 (quaternary *C*), 127.4, 127.6, 128.6, 129.4, 131.4 (quaternary *C*), 132.1 (quaternary *C*), 135.4 (quaternary *C*), 143.8 (quaternary *C*), 162.9 (*C*=O), 166.5 ppm (quaternary *C*). Elemental analysis calcd (%) for $C_{92}H_{76}N_{12}O_8Pd_4$: C, 58.09; H, 4.03; N, 8.84; found: C, 57.79; H, 4.39; N, 8.89 %.

Synthesis of Tetrakis[μ-2-[2-[2-methanidyl-κ*C*-3-[(4-methoxyphenyl)methyl]benzimidazolium-1-yl]acetyl]azanidyl-κ*N*-phenolato-κ*O*]tetrapalladium (3g)

The complex was prepared with a similar procedure to that of **3f**. A mixture of $PdCl_2$ (0.046 g, 0.25 mmol), **Lg** (0.10 g, 0.25 mmol) and K_2CO_3 (0.14 g, 1.0 mmol) was used. A orange solid was obtained. Yield: 0.049 g (39 %). M.p. = 249.5–249.9 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 1.96–2.00 (m, 4H, PdCH_aH_b), 2.12–2.17 (m, 4H, PdCHa*H*b), 3.75 (s, 12H, CH_3), 4.63 (ABq, Δ_{AB} = 18.7 Hz, J_{AB} = 15.0 Hz, 8H, CH_2), 4.86 (d, ^2J(HH) = 18.0 Hz, 4H, CH_aH_b), 5.13 (d, ^2J(HH) = 15.0 Hz, 4H, CH_aH_b), 6.45–6.55 (m, 8H, Ar *H*), 6.69 (d, ^3J(HH) = 9.0 Hz, 8H, Ar *H*), 6.82–6.94 (m, 8H, Ar *H*), 7.04–7.21 (m, 4H, Ar *H*), 7.29–7.39 (m, 8H, Ar *H*), 7.58 (d, ^3J(HH) = 9.0 Hz, 4H, Ar *H*), 8.06 (d, ^3J(HH) = 9.0 Hz, 4H, Ar *H*), 8.13 ppm (d, ^3J(HH) = 9.0 Hz, 4H, Ar *H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 29.7 (Pd*C*H$_2$), 47.6 (two overlapping *C*H$_2$), 51.3 (O*C*H$_3$), 110.9, 111.2, 115.9, 116.2, 116.3, 118.3, 121.7, 124.5 (quaternary *C*), 124.8 (quaternary *C*), 125.0, 129.0, 129.1, 131.2 (quaternary *C*), 131.9 (quaternary *C*), 143.3 (quaternary *C*), 159.8 (quaternary *C*), 164.2 (*C*=O), 166.3 ppm (quaternary *C*). Elemental analysis calcd (%) for $C_{96}H_{84}N_{12}O_{12}Pd_4$: C, 57.02; H, 4.19; N, 8.31; found: C, 57.33; H, 3.85; N, 8.62 %.

General Procedure for Mizoroki−Heck Reaction

In a typical reaction, a mixture of aryl halide (1 mmol), styrene (1.4 mmol), base (1.1 equiv), and palladium catalyst (0.2–0.02 mol% Pd atom loading) in TBAB (2 g) was stirred at 140 °C for an appropriate period of time (2−16 h). After the reaction was cooled, the product was extracted with ethyl ether (3×10 mL) and the organic layer was dried with anhydrous $MgSO_4$. The solvent was removed completely under high vacuum to give a crude product. NMR yield of the crude product was determined by using 1,3,5-trimethoxybenzene as internal standard. The pure product was isolated by column chromatography.

Single-crystal X-ray Diffraction

Samples were collected at 150(2) K on a Bruker APEX II equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (ë = 0.71073 Å). The unit cell parameters were obtained by least-squares refinement. Data collection and reduction were performed using the Bruker APEX2 and SAINT software.[23] Absorption corrections were performed using the SADABS program.[24] All the structures were solved by direct methods and refined by full-matrix least squares methods against F^2 with the SHELXTL software package.[25] All non-H atoms were refined anisotropically. All H atoms were fixed at calculated positions and refined with the use of a riding model. The structure of **3c** contained disordered CH_2Cl_2 molecules, which were unable to be modeled. The structural factor contributions from solvents were corrected using the Squeeze[26] procedure in Platon,[27] leaving a total solvent accessible void volume of 2,536 Å (589 electrons). This volume is in a good agreement of the presence of three CH_2Cl_2 molecules per molecule of **2c** (643 Å, 147 electrons). CCDC files 1845482 (**1d**), 1845487 (**2b**), and 1845488 (**2c**) contain 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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FULL PAPER

Tetranuclear Palladium Complexes of Abnormal *N*-Heterocyclic Carbene Ligands and their Catalytic Activities in Mizoroki-Heck Coupling Reaction of Electron-Rich Aryl Chlorides

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