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Chelating Bis-N-heterocyclic Carbene–Palladium(II) Complexes for Oxidative Arene C–H Functionalization

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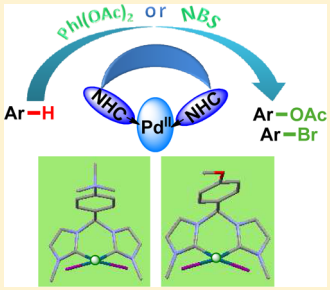
Supporting Information

ABSTRACT: Bis-N-heterocyclic carbene (NHC)-chelated palladium(II) complexes have been synthesized, characterized fully including single-crystal X-ray structural analyses, and utilized for the first time toward catalytic oxidative C–H functionalization of arenes with $PhI(OAc)_2$ and *N*-bromosuccinimide.



INTRODUCTION

The selective functionalization of unactivated arene and alkane C–H bonds to valuable organic derivatives has been a challenging research area in organometallic catalysis for a long time.[1] In this context, more recently, the oxidative functionalization approach, involving high-valent palladium intermediates (Pd^{IV} and Pd^{III}) in the catalytic cycles, has attracted considerable attention owing to its successful demonstration in the halogenation, acetoxylation, and other functionalization reactions of alkanes and arenes.[2,3] The key to the success of the above oxidative catalysis is the stability of high-valent palladium species (e.g., Pd^{IV}) in the catalytic cycles under oxidizing (and acidic) conditions. The stereoelectronic properties of the ancillary ligands play an important role in stabilizing such high oxidation states of the metal center. Palladium complexes with a chelating bis-N-heterocyclic carbene (NHC) ligand framework[4] seem to be ideal candidates with regard to the design of desirable catalysts. This is because of the following factors: (i) due to strong σ-donating ability, NHCs would facilitate oxidative addition at palladium(II) with the oxidant and also stabilize the octahedral d^6-Pd^{IV} center via efficient $\sigma(sp^2)_{carbene} \rightarrow \sigma(e_g)_{Pd}$ donation; (ii) the bis-NHC scaffold would impart extra stability to Pd^{IV} via chelation; (iii) NHC ligands possess high stability under strong oxidizing and acidic conditions (as required for oxidative transformations); and (iv) metalated NHCs are less prone to competitive reductive elimination from the Pd^{IV} intermediates and would thus favor desired functionalization reaction.[5] Strassner et al. effectively utilized the above features in designing a family of chelated palladium(II)-bis-NHC complexes and demonstrated elegant examples of oxidative trifluoroacetoxylation of methane and propane with a $K_2S_2O_8/CF_3COOH$ reagent system (Figure 1).[6] Hou et al. succeeded in achieving a regioselective trifluoroacetoxylation of *n*-propyl and *n*-octyl esters by utilizing similar palladium(II)-bis-NHC catalysts (Figure 1).[7] Recently, Kraft et al. advanced one more step and actually synthesized (bis-NHC)$Pd^{IV}Cl_4$ complexes for further direct chlorination of aromatic and aliphatic C–H bonds, albeit in a stoichiometric manner (Figure 1).[8] In a similar study, Arnold and Sanford also implemented a chelating anionic alkoxy-tethered NHC ligand to achieve Pd^{II}/Pd^{IV}-based aromatic C–H halogenations.[5] In parallel to the alkane activation, oxidative functionalization of arene C–H bonds is another highly demanding transformation. Although palladium(II) complexes with other ligand systems

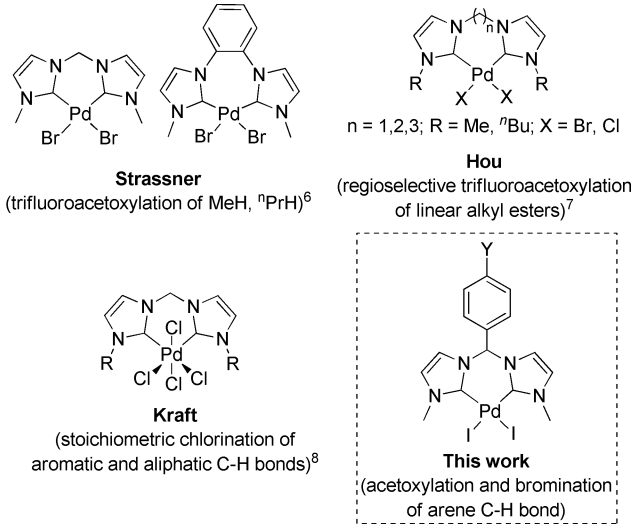


Figure 1. Application of chelated bis-NHC scaffold for oxidative $Pd^{II}/^{IV}$-based stoichiometric and catalytic C–H bond functionalization.

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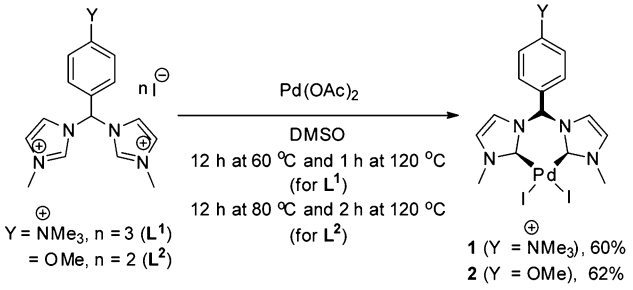
(mainly pyridine-based) including mono-NHCs have been previously used for direct acetoxylation of arenes,[9] the application of the above-described bis-NHC strategy in this transformation is yet to be executed. Motivated by this background, herein we report the first efforts in the exploration of the strategy of utilizing bis-NHC-chelated palladium(II) complexes for catalytic oxidative functionalization of arene C−H bonds (Figure 1).

RESULTS AND DISCUSSION

The chelated bis-NHC palladium(II) complexes **1** and **2** were synthesized from the corresponding imidazolium salts (L^1 and L^2) in good yields via the reaction with $Pd(OAc)_2$ in dimethyl sulfoxide solvent in a controlled manner, as shown in Scheme 1.

Scheme 1. Synthesis of the Pd(II) Complexes 1 and 2



Characterization of the complexes was achieved by ^1H and $^{13}C\{^1H\}$ NMR as well as 2D NMR spectroscopy, high-resolution electron-spray ionization mass spectrometric (ESIMS) methods, and elemental analyses (see Experimental Section). The ^1H NMR spectra of complexes **1** and **2** disclosed the absence of the imidazolium proton signals indicating metalation. The $^{13}C\{^1H\}$ NMR spectra of the complexes exhibited the carbenic carbon ($Pd-C_{carbene}$) signals at 166.3 ppm (for **1**) and 162.1 ppm (for **2**), respectively.[10] Both the complexes were further unambiguously characterized by single-crystal X-ray diffraction analyses. As depicted in Figure 2, the molecular structures of **1** and **2** confirmed the usual square planar geometry around the d^8-Pd^{II} center with a slight distortion. The bidentate coordination mode of the bis-NHC ligand to the palladium center generated a six-membered metallacycle with a boat conformation. The chelates exhibited

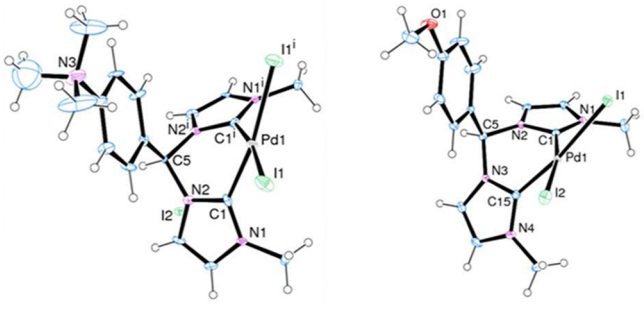
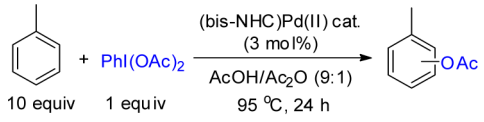


Figure 2. ORTEP diagrams of complexes **1** (left) and **2** (right) (30% ellipsoid probability level). Selected bond lengths (Å) and bond angles (deg): Complex **1**: C1−Pd1 = 1.988(12); Pd1−C1i = 1.988(12); Pd1−I1 = 2.6637(13); C1i−Pd1−C1 = 83.0(7); I1−Pd1−I1i = 94.01(6). Complex **2**: C1−Pd1 = 1.987(4); C15−Pd1 = 1.982(4); Pd1−I1 = 2.6474(4); Pd1−I2 = 2.6528(4); C15−Pd1−C1 = 83.38(16); I1−Pd1−I2 = 93.105(14).

$C_{carbene}-Pd^{II}-C_{carbene}$ bite angles of 83.0(7)° (for **1**) and 83.38(16)° (for **2**), which resulted in $I-Pd^{II}-I$ bond angles of 94.01(6)° (for **1**) and 93.105(14)° (for **2**). The $Pd^{II}-C_{carbene}$ bond distances in **1** and **2** were 1.988(12) and ∼1.987(4) Å, respectively. The other bond lengths and bond angles were typical of Pd^{II}−bis NHC complexes.[11]

As NHCs are known to exert strong σ-donating influence to the metal centers in their complexes, it is expected that these palladium complexes would undergo an easy oxidation to generate highly electrophilic Pd^{IV} species, conducive for facile C−H activation, under oxidative catalysis conditions. First we selected acetoxylation of arene C−H bonds to explore the above opportunity using reported catalytic conditions.[5,9a] The model acetoxylation reaction of toluene (10 equiv) with $PhI(OAc)_2$ (1 equiv) at 95 °C in a $AcOH/Ac_2O$ (9:1) solvent mixture revealed that 3 mol % of complex **1** or **2** afforded ∼52−58% yield of the product after 24 h (Scheme 2). With the use of

Scheme 2. Catalytic C−H Acetoxylation of Toluene by Complexes 1 and 2



Yield = 52% with cat. **1**; 58% with cat. **2**

a 1:1 molar ratio of toluene and $PhI(OAc)_2$, the reaction did not proceed to yield any acetoxylated product, whereas the other molar ratios of toluene/$PhI(OAc)_2$ (5:1 and 15:1) led to a decreased yield of the product (see Supporting Information). However, the regioisomeric distribution of acetoxylated toluene was found to be unchanged in all these cases. The acetoxylation reaction did not proceed in solvent like acetonitrile. Similarly, the yield of the acetoxylated product was found to be reduced when the reaction was run for less than 24 h (Figure S28, Supporting Information). A comparative catalytic acetoxylation of toluene performed with complex **2**, a model Strassner's complex [(NHC-CH_2-NHC)PdI_2], and $Pd(OAc)_2$ as catalysts indicated that complex **2** was a marginally better catalyst (see Supporting Information for details). Hence, with 3 mol % loading of catalyst **1** and catalyst **2**, we explored other arene molecules for catalytic C−H functionalization with $PhI(OAc)_2$ as oxidant (Table 1). There was a marginal increase in the yields with anisole as substrate. The regioisomeric ratio (*ortho*/*meta*/*para*) of the acetoxylated products was clearly regulated by the inductive and mesomeric effects of the functional groups present in the substrate. In order to verify the effect of a directing group on the regioselectivity of the products, 2-phenylpyridine and acetophenone were employed. As expected, a single regioisomer (*ortho*) was obtained in these cases, which indicated that the pyridine and carbonyl functionalities must have coordinated to the metal center, thus making it difficult for the formation of multiple isomers. The catalysts showed poor reactivity with an unactivated substrate (benzene). We further tested this oxidative C−H functionalization protocol with *N*-bromosuccinimide (NBS) as oxidant, and some preliminary results showed that NBS could also be utilized for the same (Table 1). Both complexes **1** and **2** were found to be active in bromination of only the substrates with directing groups. The yields were found to be moderate to good.

To gain some insight into the mechanistic steps, we conducted a series of control experiments (Scheme 3). It was

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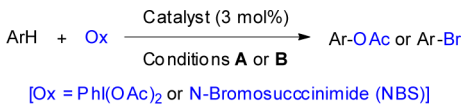
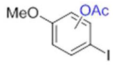
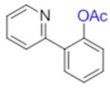
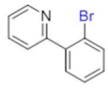
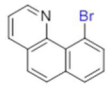
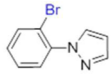
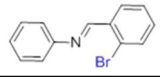
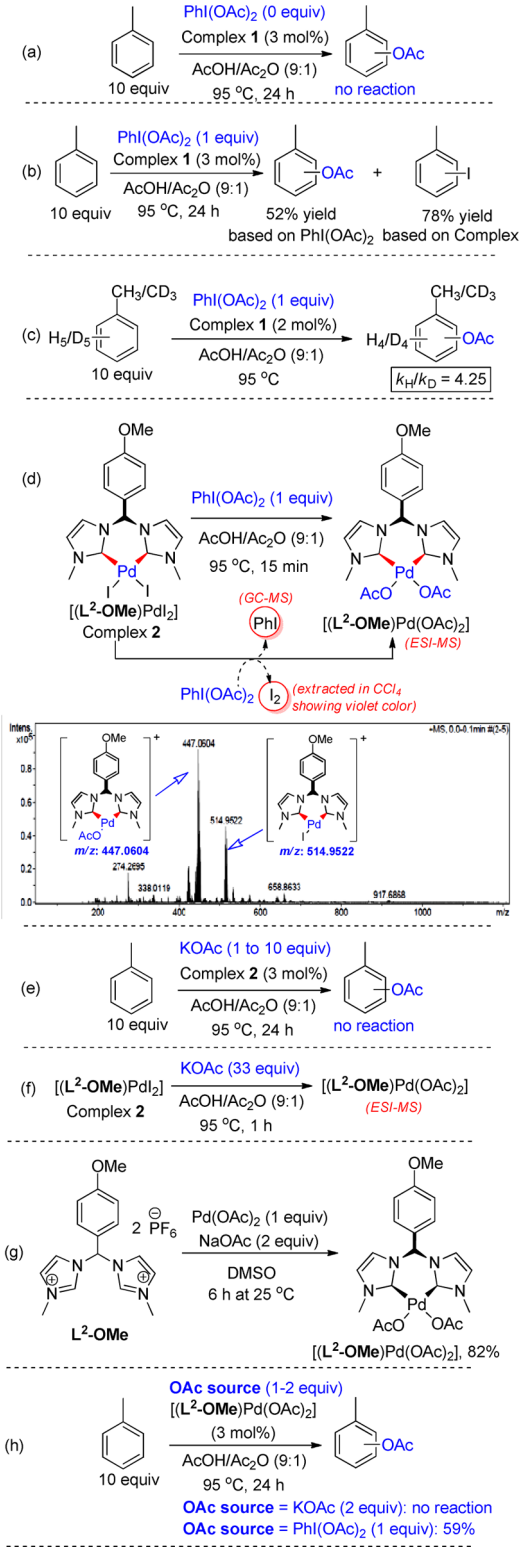
Table 1. (Bis-NHC)Pd(II)-Complex-Catalyzed Acetoxylation and Bromination of Arenes[a]



#	ArH	ArOAc/ArBr	Yield (%) cat. 1/cat 2
1	Toluene		52/58[b]
2	Ethylbenzene		41/46[c]
3	Anisole		62/56[d]
4	4-Iodoanisole		54/51[e]
5	Benzene		14/31
6	Acetophenone		43/38
7	2-Phenylpyridine		56/58
8	Acetophenone		22/18
9	2-Phenylpyridine		44/53
10	Benzo[*h*]quinoline		14/12
11	1-Phenylpyrazole		65/73
12	*N*-Benzylideneaniline		48/53

[a]Reaction conditions **A**: ArH (10 mmol), $PhI(OAc)_2$ (1 mmol), bis-NHC-Pd(II) catalyst (complex **1** or complex **2**) (0.03 mmol), $AcOH/Ac_2O$ (1 mL; 9:1, v/v), 95 °C, 24 h. Reaction conditions **B**: ArH (10 mmol), NBS (1 mmol), bis-NHC-Pd(II) catalyst (complex **1** or complex **2**) (0.03 mmol), CH_3CN (1 mL), 95 °C, 24 h. Yields were calculated by GCMS using chlorobenzene as internal standard added after the reaction was over. [b]*Ortho/meta/para*: 1.2/1.0/1.3. [c]*Ortho/meta/para*: 1.16/1.0/1.44. [d]*Ortho/meta/para*: 1.1/1.0/1.9. [e]2-/3-Isomeric mixture.

Scheme 3. Control Experiments



observed that in the absence of oxidant the reaction did not yield any functionalized product (Scheme 3a), indicating the oxidative nature of the catalysis. An important observation of the formation of iodotoluene (trace amount based on toluene, but 78% based on catalyst **1**) along with the desired acetoxylated product, in the catalytic reaction of toluene with $PhI(OAc)_2$ by complex **1**, provided a strong indication in favor of the formation of an "Ar–Pd^{IV}–I" intermediate during the catalysis (Scheme 3b). This Pd^{IV} intermediate was possible to generate via oxidation of $(NHC)_2Pd^{II}(I)_2$ by $PhI(OAc)_2$ followed by acetate-assisted aryl C–H activation with the resulting $(NHC)_2Pd^{IV}(OAc)_2(I)_2$ intermediate. A similar observation was also reported by Cárdenas et al.[9a] The involvement of the C–H bond-breaking reaction in the rate-determining step of the catalysis was indicated by the intermolecular kinetic isotope effect (KIE) value of 4.25

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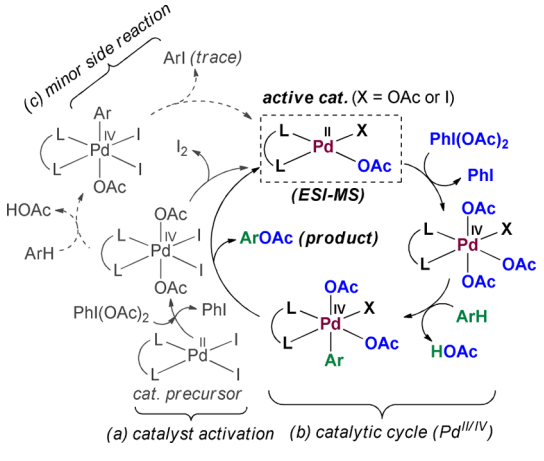
(Scheme 3c, Figure S31, Supporting Information). Next, a stoichiometric reaction using equimolar amounts of complex **2** and the oxidant $PhI(OAc)_2$ in $AcOH/Ac_2O$ (9:1, v/v) at 95 °C was performed to check the integrity and robustness of the "$(NHC)_2Pd$" coordination backbone as well as to evaluate the nature of the active catalyst during the catalysis (Scheme 3d). Analysis of the reaction mixture by GCMS indicated the presence of only iodobenzene as the organic product, which should have been generated from the oxidant $PhI(OAc)_2$ after the oxidation of palladium(II) in **2**. There was no evidence for the presence of acetoxylated-NHC ligands. The above results suggested that the "$(NHC)_2Pd$" backbone of the catalyst remained intact during catalysis under an oxidizing environment. It is noteworthy to mention here that ESIMS studies have been proved very useful in investigating the mechanistic details of palladium-catalyzed C−H acetoxylation reactions as recently demonstrated by Xu and co-workers.[12] Along the same line, the ESIMS studies of the above reaction mixture suggested the generation of an $(NHC)_2Pd(OAc)_2$ species plausibly via oxidation of the palladium(II) precursor followed by a reductive elimination of I_2 from the oxidized $(NHC)_2Pd^{IV}(OAc)_2(I)_2$ intermediate (Scheme 3d). Reductive elimination of I_2 was confirmed by extraction of I_2 from the above reaction mixture with CCl_4, which showed the characteristic violet color (see Supporting Information for details). It was further confirmed that the liberation of I_2 was not observed without oxidant under similar reaction conditions. No C−H acetoxylation was observed from the reaction of toluene with KOAc (instead of $PhI(OAc)_2$) in the presence of a catalytic amount of complex **2** under similar reaction conditions (Scheme 3e), suggesting that the present acetoxylation reaction is not a simple C−H substitution with acetate of the active species, $(NHC)_2Pd(OAc)_2$, which was found to be generated from the reaction of complex **2** with KOAc as well via anion exchange (Scheme 3f). The proposed active species, $(NHC)_2Pd(OAc)_2$, was independently synthesized and characterized by NMR spectroscopic and ESI-MS techniques (Scheme 3g; see Supporting Information for details). Control catalytic experiments by using KOAc and $PhI(OAc)_2$ as acetoxylating agents suggested again that in the presence of oxidizing agent ($PhI(OAc)_2$) only, C−H acetoxylation catalysis was successful (Scheme 3h).

Based on the above control studies and available literature reports,[3,5,9,12] a plausible catalytic cycle is shown in Scheme 4.

Scheme 4. Plausible Catalytic Cycle



The activation of the catalyst precursor $(NHC)_2Pd(I)_2$ to generate active $(NHC)_2Pd(OAc)_2$ species could occur via oxidation by $PhI(OAc)_2$ to $(NHC)_2Pd(I)_2(OAc)_2$ followed by a reductive elimination of I_2 (Scheme 4a).[13] It is rational to hypothesize that the metal center in $(NHC)_2Pd(OAc)_2$, being electron-rich through coordination by strong σ-donor NHC ligands, undergoes oxidation prior to C−H activation, to result in the Pd^{IV} intermediate $(NHC)_2Pd(OAc)_4$ (Scheme 4b). Next, an acetate-assisted electrophilic C−H activation of arene by the Pd^{IV} center generated a Pd^{IV}−aryl intermediate, well-poised for the reductive elimination of the product ArOAc. The generation of the trace amount of iodoarene side product during catalysis could be explained by a similar acetate-assisted electrophilic C−H activation of arene by the Pd^{IV} center in $(NHC)_2Pd(I)_2(OAc)_2$ followed by reductive elimination of ArI (Scheme 4c). Although no Pd^{IV} intermediate complex could be isolated from the reaction and a Pd^{II}/Pd^0 cycle cannot be ruled out completely, all the experimental results of the control studies suggested the involvement of a Pd^{II}/Pd^{IV} cycle under the present catalytic conditions.

CONCLUSIONS

In summary, we have reported the synthesis of two bis-NHC-chelated palladium(II) complexes, which were characterized fully including single-crystal X-ray structures. These bis-NHC-Pd^{II} complexes have been demonstrated for the first time in oxidative arene C−H bond functionalization catalysis with $PhI(OAc)_2$ and NBS as oxidants. Plausible catalytic steps have been proposed based on some key control experiments, which suggested the involvement of a Pd^{II}/Pd^{IV} cycle during catalysis. Improvement of the catalytic performance through efficient ligand design will be the subject of future work.

EXPERIMENTAL SECTION

I. General Methods and Materials. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AVANCE III 400 and 700 MHz NMR spectrometers at room temperature unless mentioned otherwise. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard (DMSO: δ = 2.50 ppm for ^1H spectra, 39.5 ppm for $^{13}C\{^1H\}$ spectra; acetone: δ = 2.05 ppm for ^1H spectra, 206.3 and 29.8 ppm for $^{13}C\{^1H\}$ spectra; CH_3CN: δ = 1.94 ppm for ^1H spectra, 118.3 and 1.3 ppm for $^{13}C\{^1H\}$ spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for $^1H-^1H$ couplings unless mentioned otherwise. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), and m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. Dry solvents and reagents were obtained from commercial suppliers and used without further purification. Deuterated solvents were purchased from Aldrich. [(4-*N*,*N*′ Dimethylaminobenzene)bis(imidazaloyl)methane] and [(4-methoxybenzene)bis(imidazaloyl)methane] were prepared by following a reported procedure (see Supporting Information).[14]

II. Synthetic Procedures. *Ligand Precursor L*[1]. A round-bottom flask was charged with a mixture of [(4-*N*,*N*′-dimethylaminobenzene)-bis(imidazaloyl)methane] (80 mg, 0.3 mmol) and iodomethane (55.9 μL, 0.9 mmol) under a nitrogen atmosphere. Acetonitrile (1 mL) was added to the flask, and the reaction mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC (CH_2Cl_2/CH_3OH, 9:1 (v/v)). After the completion of the reaction, the solvent was removed by suction filtration, and the product was washed several times with diethyl ether. The solid was dried under vacuum. Yield: 190 mg (92%). ^1H NMR (400 MHz, [D_6]DMSO): δ 9.42 (s, 2H, CH_{imz}), 8.57 (s, 1H, NC*H*N), 8.18 (d, $^3J_{H-H}$ = 9.1 Hz, 2H, CH_{arom}), 8.00 (s, 2H, CH_{imi}), 7.96 (s, 2H, CH_{imi}), 7.74 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, CH_{arom}), 3.92 (s, 6H, $CH_{Me\text{-}imi}$), 3.67 ppm (s, 9H, CH_{NMe3}). $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ 148.9,

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138.2, 132.8, 129.7, 125.3, 121.9, 120.9, 70.6, 56.6, 36.5 ppm. Anal. Calcd for $C_{18}H_{26}I_3N_5$: C, 31.19; H, 3.78; N, 10.10. Found: C, 31.10; H, 3.75; N, 10.02.

Ligand Precursor L². A round-bottom flask was charged with a mixture of [(4-methoxybenzene)bis(imidazaloyl)methane] (44 mg, 0.17 mmol) and iodomethane (107.8 μL, 1.73 mmol) under a nitrogen atmosphere. Acetonitrile (0.5 mL) was added to the flask, and the reaction mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC (CH_2Cl_2/CH_3OH, 9:1 (v/v)). After the completion of the reaction, the mixture was added in a dropwise manner to a round-bottom flask containing diethyl ether. The precipitate thus formed was collected by suction filtration and was washed quickly with 1 mL of ice-cold dichloromethane. Finally, the solid was dried under vacuum. Yield: 67 mg (70%). ^{1}H NMR (400 MHz, CD_3CN): δ 9.24 (s, 2H, CH_{imi}), 8.60 (s, 1H, NC*H*N), 7.76 (t, J_{H-H} = 1.9 Hz, 2H, CH_{imi}), 7.57 (t, J_{H-H} = 1.9 Hz, 2H, CH_{imi}), 7.48 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, CH_{arom}), 7.13 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, CH_{arom}), 3.93 (s, 6H, CH_{Me-imi}), 3.88 ppm (s, 3H, CH_{OMe}). $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ 163.0, 138.4, 130.6, 126.2, 122.7, 122.2, 116.1, 72.8, 56.5, 37.8 ppm. Anal. Calcd for $C_{16}H_{20}I_2N_4O.H_2O$: C, 34.55; H, 3.99; N, 10.07. Found: C, 34.82; H, 3.94; N, 10.01.

Complexes 1 and 2. $Pd(OAc)_2$ (23.3 mg, 0.1 mmol) and ligand precursor L^1 (68 mg, 0.1 mmol) or L^2 (56 mg, 0.1 mmol) were charged into a Schlenk flask. The flask was evacuated and subsequently filled with argon gas three times. Under this condition, 5 mL of degassed DMSO was added to the flask. The mixture was initially stirred at room temperature for 1 h and then at 60 °C for 12 h (in the case of **1**) or at 80 °C for 12 h (in the case of **2**) and at 120 °C for 1 h (in the case of **1**) or at 120 °C for 2 h (in the case of **2**) more. The reaction mixture was cooled, and the solvent was removed through vacuum distillation (at 60 °C). The solid thus obtained was collected by suction filtration and washed with water, ether, and ice-cold dichloromethane. Then the product was dried under vacuum. Complex **1**: yield 40 mg (60%). ^{1}H NMR (400 MHz, CD_3CN): δ 8.46 (s, 1H, NC*H*N), 8.06 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, CH_{imi}), 8.02 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, CH_{arom}), 7.68 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, CH_{arom}), 7.38 (d, $^3J_{H-H}$ = 1.9 Hz, 2H, CH_{imi}) 3.96 (s, 6H, CH_{Me-imi}), 3.88 ppm (s, 9H, CH_{NMe3}). $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]acetone): δ 166.3, 141.5, 130.8, 123.9, 123.0, 121.6, 75.4, 58.1, 30.6 ppm (one peak was not observed). HRMS (ESI, positive ion): $[M]^+$ = 669.9179 (calculated as 669.9157 for $[C_{18}H_{24}I_2N_5Pd]^+$). Anal. Calcd for $C_{18}H_{24}I_3N_5Pd{\cdot}CH_3SOCH_3$: C, 27.43; H, 3.45; N, 8.00. Found: C, 27.25; H, 3.47; N, 8.03. Complex **2**: yield 35 mg (53%). ^{1}H NMR (400 MHz, [D_6]DMSO): δ 7.95−7.80 (m, 3H, CH_{imi}+NC*H*N), 7.53−7.24 (m, 4H, CH_{imi}+CH_{arom}), 6.98 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, CH_{arom}), 3.89 (s, 6H, CH_{Me-imi}), 3.77 ppm (s, 3H, CH_{OMe}). $^{13}C\{^1H\}$ NMR (100 MHz [D_6]DMSO): δ 162.1, 159.5, 129.2, 128.1, 123.3, 122.2, 113.7, 74.3, 55.3, 40.7 ppm. HRMS (ESI, positive ion): $[M]^+$ = 514.9506 (calculated as 514.9561 for $[C_{16}H_{18}IN_4OPd]^+$). Anal. Calcd for $C_{18}H_{24}I_3N_5Pd{\cdot}0.25CH_3SOCH_3$: C, 29.93; H, 2.97; N, 8.46. Found: C, 29.69; H, 3.00; N, 8.48.

III. Single-Crystal X-ray Diffraction Analysis. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at different low temperatures for each crystal. Structures were solved with direct methods using SHELXS-97 and refined with full-matrix least-squares on F^2 using SHELXL-97.[15] Full crystallographic data of **1** (CCDC 1034491) and **2** (CCDC 1034492) can be obtained free of charge from the Cambridge Crystallographic data Center via www.ccdc.cam.ac.uk/data_request/cif.

IV. General Procedure for the Catalytic Oxidative Acetoxylation of Toluene with Complexes 1 and 2. Diacetoxyiodobenzene (40.4 mg, 0.125 mmol), catalyst (varying amounts), and toluene (1.25 mmol) were placed in a sealed tube that was equipped with a magnetic bar. One milliliter of freshly prepared acetic acid/acetic anhydride (9:1 v/v) mixed solvent was added to the mixture. The reaction mixture was stirred at 95 °C for 24 h. It was then cooled to room temperature, and the yield was calculated by GCMS analysis using PhCl as an internal standard added after the reaction was over.

V. General Procedure for the Catalytic Oxidative Acetoxylation and Bromination of Arenes with Complexes 1 and 2. *Acetoxylation:* Diacetoxyiodobenzene (40.4 mg, 0.125 mmol), complex **1** (2.96 mg, 0.00375 mmol), or complex **2** (2.40 mg, 0.00375 mmol) and the arene (1.25 mmol) were placed in a sealed tube that was equipped with a magnetic bar. One milliliter of freshly prepared acetic acid/acetic anhydride (9:1 v/v) was added to the mixture. The reaction mixture was stirred at 95 °C for 24 h. It was then cooled to room temperature, and the yield was calculated by GCMS analysis using PhCl as an internal standard added after the reaction was over.

Bromination: N-Bromosuccinimide (22.2 mg, 0.125 mmol), complex **1** (2.96 mg, 0.00375 mmol) or complex **2** (2.40 mg, 0.00375 mmol), and the arene (1.25 mmol) were placed in a sealed tube, which was equipped with a magnetic bead. One milliliter of acetonitrile was added to the mixture. The reaction mixture was stirred at 95 °C for 24 h. It was then cooled to room temperature, and the yield was calculated by GCMS analysis using PhCl as an internal standard added after the reaction was over.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H, $^{13}C\{^1H\}$, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and HMBC NMR spectra; ESI mass spectra; additional text; CIF files of complexes **1** (CCDC 1034491) and **2** (CCDC 1034492). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/om501163m.

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Notes

The authors declare no competing financial interest.

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