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Cyclometalations on the Imidazo[1,2-*a*][1,8]naphthyridine Framework

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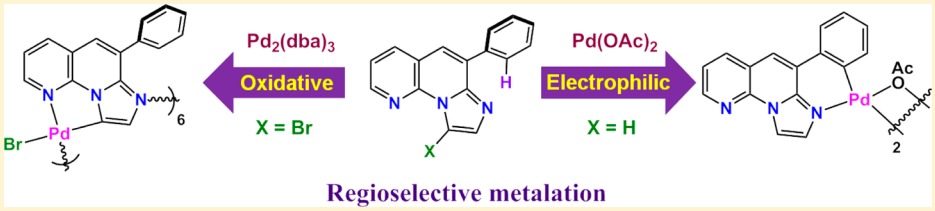
Supporting Information



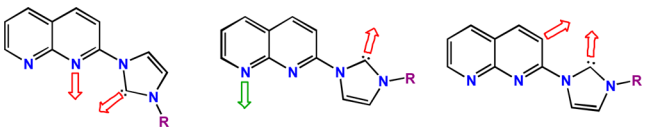
ABSTRACT: Cyclometalation on the substituted imidazo[1,2-*a*][1,8]naphthyridine platform involves either the C_3-aryl or C_4'-aryl *ortho* carbon and the imidazo nitrogen N_3'. The higher donor strength of the imidazo nitrogen in comparison to that of the naphthyridine nitrogen aids regioselective orthometalation at the C_3/C_4'-aryl ring with Cp^*Ir^{III} (Cp^* = η^5-pentamethylcyclopentadienyl). A longer reaction time led to double cyclometalations at C_3-aryl and imidazo C_5'-H, creating six- and five-membered metallacycles on a single skeleton. Mixed-metal Ir/Sn compounds are accessed by insertion of $SnCl_2$ into the Ir−Cl bond. $Pd(OAc)_2$ afforded an acetate-bridged dinuclear ortho-metalated product involving the C_3-aryl unit. Metalation at the imidazo carbon (C_5') was achieved via an oxidative route in the reaction of the bromo derivative with the Pd(0) precursor $Pd_2(dba)_3$ (dba = dibenzylideneacetone). Regioselective C−H/Br activation on a rigid and planar imidazonaphthyridine platform is described in this work.

INTRODUCTION

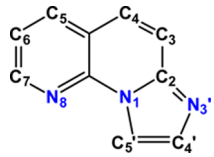
The utility of 1,8-naphthyridine (NP) ligands for a wide range of applications, including axial C−H bond activation[1] and C−C bond formation on metal−metal-bonded complexes,[2] bimetallic[3] and bifunctional catalysis,[4] and construction of self-assembled inorganic architectures,[5] has been demonstrated in recent years. Functionalization of imidazole with different naphthyridines provided ligands that afford discrete dinuclear complexes, tetranuclear metallamacrocycles, and polymeric chain compounds with the $Rh^I(COD)$ unit.[6] Naphthyridine-functionalized N-heterocyclic carbenes (NHCs) exhibit topological flexibility and form complexes with a variety of metal components (Scheme 1).[7]

We sought to develop ligand systems based on fused imidazo[1,2-*a*][1,8]naphthyridine, illustrated in Scheme 2. The purpose was to employ it as a cyclometalating ligand and also to access a precursor for an abnormal NHC ligand upon quaternization of imidazolyl nitrogen.[8] Initial use of Cp^*Ir^{III}

Scheme 1. Multifaceted Naphthyridine-Functionalized N-Heterocyclic Carbenes



Scheme 2. Imidazo[1,2-*a*][1,8]naphthyridine and Atom-Numbering Scheme



led to orthometalation involving the phenyl substituent at C_4' and the imidazo nitrogen N_3'. Relocating the phenyl substituent from the C_4' to the C_3 position afforded a six-membered cyclometalated ring system. A second cyclometalation at C_5' could only be achieved upon carrying out the reaction for a longer duration. Although facile cyclometalation occurs with $Pd(OAc)_2$ involving N_3' and the phenyl unit at C_3, activation of C_5'−H could not be accomplished under normal cyclometalating conditions. Oxidative cleavage of C_5'−Br with zero-valent Pd followed by N_3' coordination gave a cyclic cyclometalated Pd_6 framework. This report describes an interesting account of cyclometalation reactions on the imidazo[1,2-*a*][1,8]naphthyridine platform.

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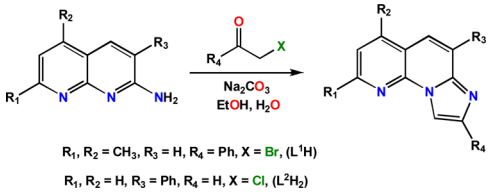
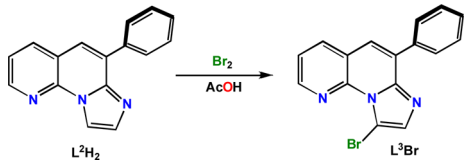
RESULTS AND DISCUSSION

Cyclometalation with Cp*Ir^{III}. Imidazo[1,2-*a*][1,8]-naphthyridines L^1H and L^2H_2 are synthesized by condensation of the appropriate 2-aminonaphthyridine derivatives with *α*-halogenocarbonyl compounds (Scheme 3).[9] L^3Br is synthesized by the treatment of L^2H_2 with liquid bromine in acetic acid at room temperature (Scheme 4).

Scheme 3. Synthesis of L^1H and L^2H_2



Scheme 4. Synthesis of L^3Br



Typical cyclometalation reactions were carried out in dichloroethane (DCE) with excess NaOAc under reflux conditions. Treatment of 0.5 equiv of $[IrCp^*(\mu\text{-}Cl)Cl]_2$ with 5,7-dimethyl-4′-phenylimidazo[1,2-*a*][1,8]naphthyridine (L^1H) in the presence of excess NaOAc in dichloroethane at reflux for 4 h afforded *ortho* C−H activation of C_4' phenyl, resulting in the five-membered cyclometalated complex $[Cp^*Ir(Cl)L^1]$ (**1**) (Scheme 5). The ^1H NMR spectrum of **1** reveals cyclometalation with disappearance of the *ortho* proton of the phenyl ring. The ^{13}C NMR signal corresponding to the cyclometalated carbon appears downfield at δ 159.2 ppm in comparison to the free ligand. The ESI-MS of compound **1** exhibits a signal at m/z 600 (100%) which is assigned to $[\mathbf{1} - Cl]^+$ on the basis of simulated mass and isotope distribution patterns (Figure S14, Supporting Information).

The molecular structure of **1**, as shown in Figure 1, confirms that the ligand is ortho-metalated through C11 of the phenyl fragment and Cp*Ir is additionally anchored to the imidazo nitrogen N1. A chloride is coordinated (Ir1−Cl1 = 2.410(2) Å) to complete the piano-stool geometry around the metal. The Ir1−C11 and Ir1−N1 distances are 2.066(6) and 2.085(6) Å, respectively, comparable to those in reported Ir^{III} C^N-cyclometalated compounds.[10] The imidazonaphthyridine and phenyl rings adopt a planar configuration, reflecting orthometalation. Differences in distances between iridium and carbon atoms of the Cp* ligand are noted. The Ir1 exhibits a longer distance with C1 (2.236(8) Å) situated *trans* to the cyclometalated carbon C11 (∠C11−Ir1−C1 = 163°) in comparison to the other iridium−carbon distances (2.196(8)−2.143(7) Å) with Cp*.

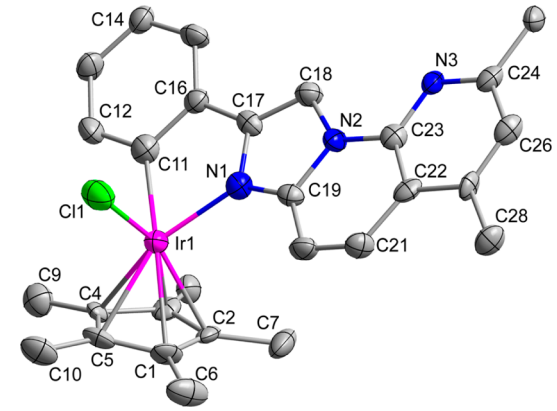
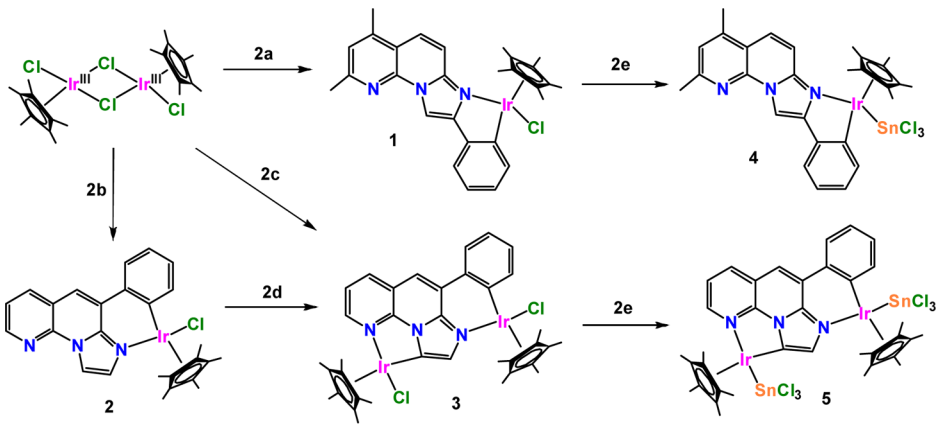


Figure 1. Molecular structure (50% probability thermal ellipsoids) of **1** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ir1−C11 = 2.066(6), Ir1−N1 = 2.085(6), Ir1−Cl1 = 2.410(2), Ir1−C3 = 2.143(7), Ir1−C2 = 2.173(7), Ir1−C4 = 2.186(7), Ir1−C5 = 2.196(8), Ir1−C1 = 2.236(8); C11−Ir1−N1 = 76.9(3), C11−Ir1−C3 = 99.3(3), C11−Ir1−C4 = 102.3(3), N1−Ir1−C2 = 98.1(3).

Scheme 5. Synthesis of 1−5



(**2a**) 2 eq. L^1H, 6 eq. NaOAc, DCE, 4h, reflux; (**2b**) 2 eq. L^2H_2, 6 eq. NaOAc, DCE, 4h, reflux; (**2c**) 1 eq. L^2H_2, 6 eq. NaOAc, DCE, 12h, reflux; (**2d**) 0.5 eq. $[IrCp^*Cl_2]_2$, 6eq. NaOAc, DCE, 12h, reflux; (2e) 1 eq. anhydrous $SnCl_2$, dichloromethane, 4h, rt.

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It was argued at this point that the *ortho* methyl group of the naphthyridine unit does not allow close approach of the bulky Cp*Ir unit to the naphthyridine nitrogen N_8. To test this hypothesis, we proposed a ligand that is devoid of *o*-methyl substituents on the naphthyridine unit. However, unsubstituted imidazonaphthyridine could not be synthesized due to lack of an easy synthetic protocol for 2-aminonaphthyridine. Instead, we synthesized 3-phenyl-2-aminonaphthyridine by Friedlander condensation of 2-aminonicotinaldehyde with benzyl cyanide.[11] Condensation of 3-phenyl-2-aminonaphthyridine with *α*-chloroacetaldehyde afforded 3-phenylimidazo[1,2-*a*][1,8]-naphthyridine (L^2H_2).

The reaction of L^2H_2 with $[IrCp^*(\mu\text{-}Cl)Cl]_2$ following a protocol identical with that followed for **1** led to the C−H cleaved product $[IrClCp^*(L^2H)]$ (**2**). The C_3 phenyl is ortho-metalated with Cp*Ir which is further anchored to the imidazo nitrogen, creating a six-membered metalacycle. The ^{1}H NMR spectrum shows multiple resonances corresponding to aromatic protons in the range δ 7.06−8.60 ppm. Two imidazo protons appear at δ 8.47 and 7.71 ppm, and Cp* protons appear as a singlet at δ 1.42 ppm. The cyclometalated carbon exhibits a resonance at 154 ppm in the ^{13}C NMR spectrum. The ESI-MS of compound **2** exhibits a signal at m/z 572 which is assigned to $[\mathbf{2} - Cl]^+$.

The molecular structure of **2** is shown in Figure 2, and important metrical parameters are provided in the correspond-

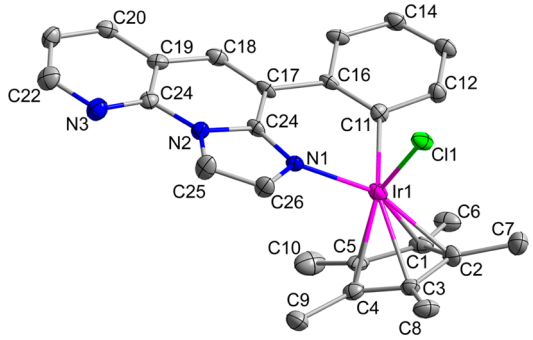

Figure 2. Molecular structure (50% probability thermal ellipsoids) of **2** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ir1−N1 = 2.054(5), Ir1−C11 = 2.054(6), Ir1−Cl1 = 2.417(1), Ir1−C5 = 2.126(6), Ir1−C1 = 2.182(6), Ir1−C2 = 2.173(6), Ir1−C4 = 2.235(6), Ir1−C3 = 2.263(6); N1−Ir1−C11 = 86.4(2), C11−Ir1−C5 = 105.9(2), N1−Ir1−C5 = 105.7(2), N1−Ir1−C1 = 143.2(2), C11−Ir1−C1 = 93.2(2), N1−Ir1−C2 = 156.8(2).

ing figure caption. The structural features of **2** are similar to those of compound **1** except that the C_3 phenyl is cyclometalated instead of the C_4' phenyl. The Ir1−C11 (cyclometalated carbon) and Ir1−N1 distances of the chelating ligand are 2.054(6) and 2.054(5) Å, respectively. Other bond parameters are comparable to those of compound **1**.

A prolonged reaction (12 h) of L^2H_2 with an equivalent amount of $[IrCp^*(\mu\text{-}Cl)Cl]_2$ in the presence of excess NaOAc in refluxing DCE afforded the double-cyclometalated product $[Ir_2Cl_2Cp_2^*(L^2)]$ (**3**). Both imidazo C_5'−H and C_3-phenyl *ortho* C−H are metalated. The same compound could be obtained by treating **2** with another 1 equiv of the metal precursor in the presence of NaOAc. The ^{1}H NMR spectrum of **3** exhibits signals very similar to those of **2** with additional cyclometalation through the imidazo carbon, indicated by the absence of one of the imidazo proton signals (δ 8.47 in **2**). The other imidazo proton signal is found at δ 7.70 ppm. The Cp* protons appear as two singlets at δ 1.84 and 1.40 ppm. The cyclometalated carbons exhibit resonances at δ 154 and 156 ppm in the ^{13}C NMR spectrum. The ESI-MS of compound **3** exhibits a signal at m/z 934 which is assigned to $[\mathbf{3} - Cl]^+$.

The double cyclometalations on a single ligand framework consisting of five- and six-membered rings have been confirmed by X-ray crystallography (Figure 3). The second cyclo-

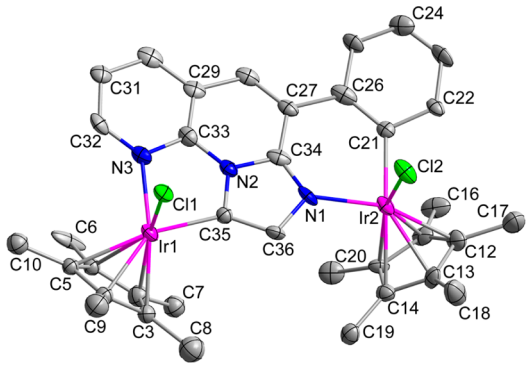

Figure 3. Molecular structure (50% probability thermal ellipsoids) of **3** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ir1−C35 = 2.019(13), Ir1−C3 = 2.085(12), Ir1−C2 = 2.097(11), Ir1−C4 = 2.155(11), Ir1−N3 = 2.155(11), Ir1−C1 = 2.173(10), Ir1−C5 = 2.208(11), Ir1−Cl1 = 2.398(4), Ir2−C21 = 2.049(13), Ir2−N1 = 2.067(12), Ir2−C12 = 2.127(16), Ir2−C11 = 2.159(14), Ir2−C15 = 2.169(13), Ir2−C13 = 2.211(15), Ir2−C14 = 2.239(14), Ir2−Cl2 = 2.416(3); C35−Ir1−N3 = 78.5(5), C35−Ir1−Cl1 = 89.0(3), C21−Ir2−N1 = 87.6(5), C21−Ir2−C11 = 95.3(5).

metalation occurs through the imidazo carbon C35 and naphthyridine nitrogen N3, creating a five-membered ring. The Ir−C(cyclometalated) distances are 2.049(13) Å (Ir2−C21) and 2.019(13) Å (Ir1−C35); Ir−N distances are 2.067(12) Å (Ir2−N1) and 2.155(11) Å (Ir1−N3). The chelate angles (∠C−Ir−N) for the five- and six-membered rings are 78.5(5) and 87.6(5)°, respectively. Two Cp* rings are positioned *syn* to each other with respect to the ligand plane. The Ir−C(Cp*) distances are slightly shorter (2.085(12)−2.208(11) Å) when the metal is part of a five-membered metallacycle in comparison to a six-membered-ring system (2.239(14)−2.416(3) Å).

We recently initiated a program to prepare mixed-metal Ir−Sn compounds based on cyclometalated organometallic constructs.[12] Insertion of $SnCl_2$ into the Ir−Cl bond in **1** proceeds efficiently, forming the mixed Ir−Sn compound $[Cp^*Ir(SnCl_3)(L^1)]$ (**4**) in high yield (93%) (Scheme 5). The ^{1}H and ^{13}C NMR spectra of **4** exhibit signals very similar to those of **1**, indicating structural correspondence between them. A similar reaction with **3** afforded the heterobimetallic cyclometalated compound **5**, where the double-cyclometalated ligand framework is unchanged and two $SnCl_2$ units readily insert into both metal−chloride bonds.

The X-ray structure of **4** confirms the insertion of $SnCl_2$ into the Ir−Cl bond (Figure 4). The overall molecular structure is similar to that of **1**, except that the chloride is replaced by a $SnCl_3$ unit. The Sn atom displays a distorted-tetrahedral environment consisting of three chlorides and one iridium. The Ir−Sn−Cl angles are larger (114.3(5)−123.1(1)°) than the

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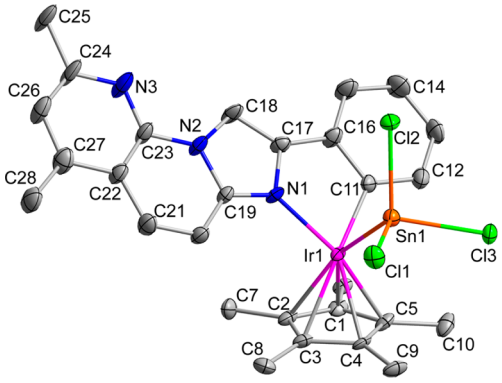


Figure 4. Molecular structure (50% probability thermal ellipsoids) of **4** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ir1−C11 = 2.076(5), Ir1−N1 = 2.082(4), Ir1−Sn1 = 2.522(1), Sn1−Cl3 = 2.378(1), Sn1−Cl2 = 2.374(1), Sn1−Cl1 = 2.374(1), Ir1−C5 = 2.171(5), Ir1−C1 = 2.195(5), Ir1−C2 = 2.205(5), Ir1−C4 = 2.224(4), Ir1−C3 = 2.251(5); C11−Ir1−N1 = 77.5(1), C11−Ir1−Sn1 = 85.3(1), N1−Ir1−Sn1 = 90.9(1), Cl2−Sn1−Cl1 = 98.1(1), Cl2−Sn1−Cl3 = 100.5(1), Cl1−Sn1−Cl3 = 96.9(1), Cl2−Sn1−Ir1 = 114.4(1), Cl1−Sn1−Ir1 = 119.4(1).

Cl−Sn1−C1 angles (96.9(1)−100.5(1)°). The Ir1−Sn1 distance is 2.522(1) Å, whereas the three Sn−Cl distances are comparable (2.374(1), 2.374(1), and 2.378(1) Å). The $SnCl_3$ unit is a weak σ donor but exhibits a large *trans* effect due to its ability to form a strong dπ−dπ bond to the metal. This is reflected in longer Ir−C(Cp*) distances (2.251(5)−2.171(5) Å) in comparison to those in **1** (2.196(8)−2.143(7) Å).

The Ir−Sn distances in **5** are 2.549(1) and 2.553(1) Å. Interestingly, two Cp* rings are positioned diagonal with respect to the ligand plane (Figure 5). This is in contrast to the *syn* orientation of Cp* units in **3**. Steric congestion involving

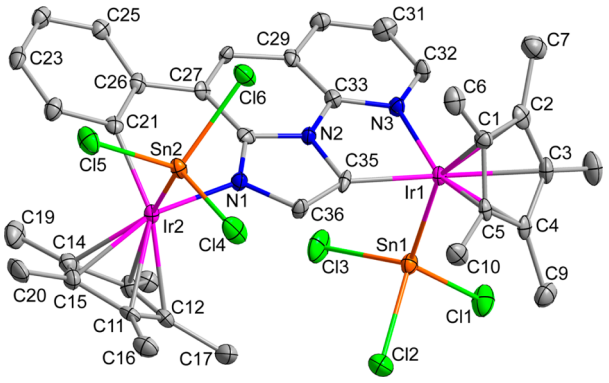
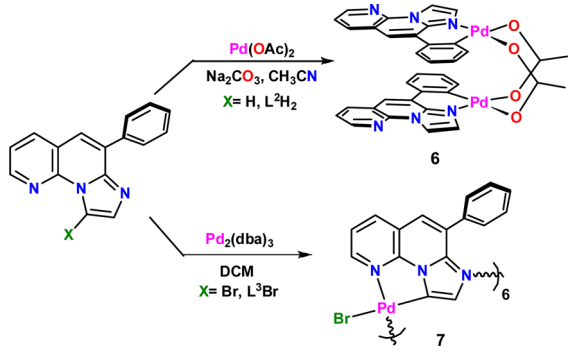


Figure 5. Molecular structure (40% probability thermal ellipsoids) of **5** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ir1−C35 = 2.068(5), Ir1−Sn1 = 2.553(1), Ir1−C4 = 2.190(5), Ir1−C1 = 2.210(5), Ir1−C2 = 2.241(5), Ir1−C3 = 2.232(5), Ir1−N3 = 2.135(4), Ir1−C5 = 2.161(5), Sn1−Cl2 = 2.368(1), Sn1−Cl3 = 2.367(1), Sn1−Cl1 = 2.374(1), Ir2−N1 = 2.059(4), Ir2−C21 = 2.087(5), Ir2−C15 = 2.189(5), Ir2−C14 = 2.226(5), Ir2−C13 = 2.217(5), Ir2−C12 = 2.246(5), Ir2− C11 = 2.241(5), Ir2−Sn2 = 2.549(1), Sn2−Cl4 = 2.385(1), Sn2−Cl6 = 2.392(1), Sn2−Cl5 = 2.403(1); C35−Ir1−N3 = 79.56(18), C35−Ir1−Sn1 = 85.10(14), N3−Ir1−Sn1 = 89.16(12), N1−Ir2−C21 = 87.42(18), N1−Ir2−Sn2 = 88.19(12), C21−Ir2−Sn2 = 89.59(14).

bulky $SnCl_3$ units is possibly responsible for an arrangement that keeps them away from each other in **5**.

Cyclopalladation. Treatment of L^2H_2 with $Pd(OAc)_2$ in acetonitrile in the presence of excess Na_2CO_3 resulted in cyclometalation of the ligand. The ^{1}H NMR spectrum of the product $Pd_2(OAc)_2(L^2H)_2$ (**6**) reveals cyclometalation by the absence of one of the *ortho* protons of the phenyl ring (Scheme 6). The methyl protons of the acetate display a sharp singlet at

Scheme 6. Synthesis of 6 and 7



δ 2.47 ppm. The ^{13}C NMR signal corresponding to the cyclometalated carbon atom appears downfield at δ 180.2 ppm. The ESI-MS of compound **6** exhibits a signal at m/z 391 (100%) which is assigned to $[M - (CH_3COO) + (CH_3CN)]^+$ on the basis of simulated mass and isotope distribution patterns.

The molecular structure of **6**, as shown in Figure 6, confirms two cyclometalated palladium units that are held in proximity by bridging acetates. Only half of the molecule is located in the asymmetric unit related to the other half by a C_2 axis that bisects the Pd···Pd vector. The ligand is cyclometalated through

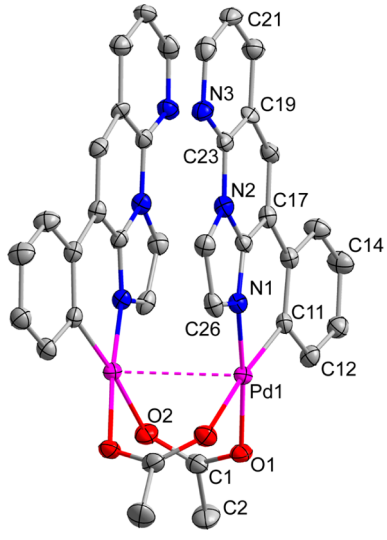


Figure 6. Molecular structure (50% probability thermal ellipsoids) of **6** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1−N1 = 1.982(3), Pd1−C11 = 1.992(4), Pd1−O1 = 2.066(3), Pd1*−O2 = 2.144(3), O1−C1 = 1.264(5), O2− C1 = 1.257(5), C1−C2 = 1.508(6), Pd1−Pd1* = 2.861(1), N1−Pd1−C11 = 91.09(14); C11−Pd1−O1 = 92.80(14), N1−Pd1−O2 = 91.03(12), N1−Pd1−O1 = 175.21(12). Symmetry code: $-x$, y, 1.5 − z.

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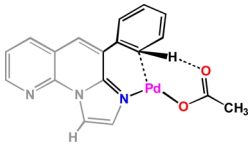
the *ortho* carbon C11 of L^2H and the imidazole nitrogen N1, creating a six-membered ring. The Pd1−C11 and Pd1−N1 distances are 1.992(4) and 1.982(3) Å, respectively, comparable with those in previously reported palladium(II) cyclometalated compounds.[13] The Pd···Pd distance of 2.861(1) Å is consistent with an expected bond order of zero,[13a] and two $\{Pd(C^{\wedge}N)\}_2$ units are spanned by two bridging acetates with Pd−O distances of 2.066(3) and 2.144(3) Å.

The acetate-assisted cyclometalation proceeds through initial coordination of $Pd(OAc)_2$ to the imidazo nitrogen (N_3') followed by the interaction of the *ortho* C−H bond with the metal. Finally, the hydrogen is transferred to the metal-bound acetate via a highly ordered six-membered transition state (Scheme 7). This proposal is in accordance with the concerted metalation−deprotonation (CMD) mechanism as proposed by Ryabov, Fagnou, and others.[14] Since the imidazo nitrogen is more basic than the naphthyridine nitrogen, this allows orthometalation of the C_3-aryl ring over the C_5' hydrogen. Regioselective cyclometalation at C_5' could not be achieved by this method, even after employing 1 equiv more of $Pd(OAc)_2$ followed by prolonged heating.

Scheme 7. Acetate-Assisted Palladation via a Six-Membered Transition State



Oxidative addition is an alternate pathway to access cyclometalated compounds.[15] Oxidative addition of the C−H bond to electron-rich, low-valent complexes of late transition metals (Re, Fe, Ru, Os, Ir, Pt) has afforded a plethora of metalated compounds.[16] Nolan and Crabtree independently proposed oxidative addition of the imidazolium C−H to Pd(0) for the synthesis of Pd^{II}−NHC compounds.[17] Cavell followed a similar procedure to isolate the metal−NHC−hydride complex $[Pt(H)(dmiy)(PR_3)_2]BF_4$ (dmiy = 1,3-dimethylimidazolin-2-ylidene and R = phenyl, cyclohexyl).[18] Albrecht also applied C−I oxidative addition in halide-substituted imidazolium salts with low-valent Pd precursors to obtain Pd−NHC complexes.[19]

To accomplish selective C_5' metalation, we employed 5′-bromo-3-phenylimidazo[1,2-*a*][1,8]naphthyridine (L^3Br). Oxidative addition of L^3Br to $Pd_2(dba)_3$ (dba = dibenzylideneacetone) affords the cyclometalated palladacycle $\{Pd(L^3)Br\}_6$ (Scheme 6). The ^{13}C NMR signal corresponding to the cyclometalated carbon appears downfield at δ 153.1 ppm. The ESI-MS exhibits a signal at m/z 392 which is assigned to $[Pd(L^3)(CH_3CN)]^+$.

The X-ray structure of **7** reveals a hexanuclear cluster with a circular topology (Figure 7).[20] The asymmetric unit is comprised of a $\{Pd(L^3)Br\}_3$ unit related to the other half by a center of inversion. The geometries around the Pd atoms are very similar, and we describe one $\{Pd(L^3)Br\}$ unit here in detail. The $\{Pd(L^3)Br\}$ unit chelates through the imidazo carbon (C31) and naphthyridine nitrogen (N4). The imidazo nitrogen N6 connects to the neighboring Pd. The square-planar geometry around Pd is completed by a bromide that arises from the oxidative cleavage of the C−Br bond. The Pd1−C31(cyclometalated) distance is 1.999(10) Å, the Pd1−N4(naphthyridine) distance is 2.076(7) Å, and the Pd1−Br1 distance is 2.502(2) Å. The imidazo nitrogen binds to the Pd center with a Pd1−N3 distance of 2.016(7) Å. Six Pd centers adopt a pseudo-chair conformation with the closest and farthest Pd···Pd distances being 6.106 and 10.296 Å, respectively (Figure S18, Supporting Information). Two neighboring imidazonaphthyridine planes are nearly perpendicular (interplanar angle 77.1°) in the hexanuclear metallamacrocycle.

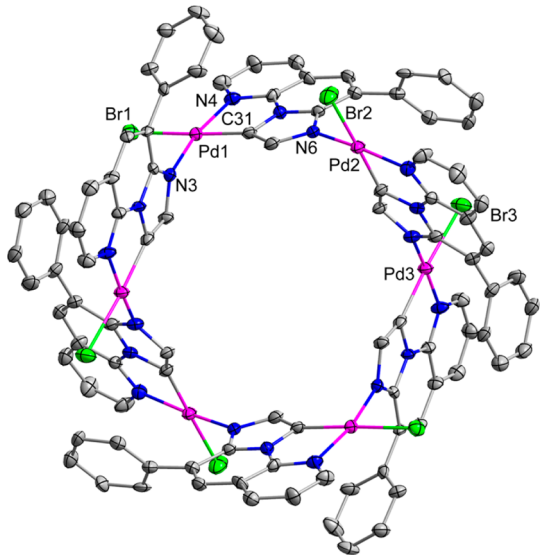


Figure 7. Molecular structure (50% probability thermal ellipsoids) of **7** with important atoms labeled. Hydrogen atoms are omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Pd1−C31 = 1.999(10), Pd1−Br1 = 2.5023(13), Pd1−N3 = 2.016(7), Pd1−N4 = 2.076(7); C31−Pd1−N4 = 82.2(3), C31−Pd1−Br1 = 175.1(2), C31−Pd1−N3 = 91.7(3), N3−Pd1−N4 = 173.1(3), N3−Pd1−Br1 = 92.9(2), N4−Pd1−Br1 = 93.1(2). Symmetry code: $-x, -y, 2 - z$.

CONCLUDING REMARKS

Owing to the superior donor ability of imidazo nitrogen, regioselective ortho C−H bond activation occurs at the C_3/C_4'-phenyl ring, affording cyclometalated Cp*Ir(C^N)Cl compounds. Double cyclometalations at C_3-aryl and C_5'-H are achieved upon prolonged heating, creating five- and six-membered metallacycles on a single platform. Insertion of $SnCl_2$ into the Ir−Cl bond afforded easy access to the corresponding mixed-metal Ir/Sn compounds. Similar to the case for Cp^*Ir^{III}, $Pd(OAc)_2$ caused regioselective orthometalation involving the C_3-aryl unit; however, C_5'-H could not be activated under similar conditions. Oxidative addition of C_5'-Br to $Pd_2(dba)_3$ allows regioselective metalation involving C_5' and the naphthyridine nitrogen N_8. Efforts are underway to access a metal-*a*NHC complex via N_3' quaternization of the cyclometalated (C_5'^N) complex, a process commonly known as post-carbene generation.[21]

EXPERIMENTAL SECTION

General Procedures. All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk-vessel and vacuum-line techniques. Glasswares were flame-dried under vacuum prior to use. Solvents were dried by conventional methods prior to use. ^1H and ^{13}C NMR spectra were obtained on JEOL JNM-LA 500 MHz spectrometers. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. ESI-MS was recorded on a Waters-Micromass Quattro Micro triple-quadrupole mass spectrometer.

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Melting points were measured in open capillaries on a JSGW melting point apparatus and are uncorrected.

Materials. Solvents were dried by conventional methods, distilled under nitrogen, and deoxygenated prior to use. $IrCl_3{\cdot}xH_2O$, $Pd(CH_3COO)_2$, and $PdCl_2$ were purchased from Arora Matthey Kolkata (India). The compounds $[IrCp^*(\mu\text{-}Cl)Cl]_2$[22] and $[Pd_2(dba)_3{\cdot}CHCl_3]$[23] were prepared according to the literature procedures. 2,4-Dimethyl-7-amino[1,8]naphthyridine, 3-phenyl-2-amino[1,8]naphthyridine, and 6,8-dimethyl-2′-phenylimidazo[1,2-*a*]-[1,8]naphthyridine (L^1H) were synthesized as reported earlier.[9]

Synthesis of L^2H_2. 3-Phenyl-2-amino[1,8]naphthyridine (165 mg, 0.74 mmol) was refluxed in ethanol/water (10/1) with a small excess of α-chloroacetaldehyde (0.2 mL, 1.10 mmol) for 4 h in the presence of an equivalent amount of Na_2CO_3 (988 mg, 1.10 mmol). After it was cooled, the solution was evaporated to dryness and the residue was chromatographed on silica and eluted with methanol/dichloromethane to give the pure product. Yield: 169 mg (92%). Mp: 105−108 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 8.72 (d, J = 4.85 Hz,1H, NP), 8.5 (s, 1H, Im), 8.20 (d, J = 7.45 Hz, 1H, NP), 7.98 (d, J = 9.15 Hz, 2H, Ph. NP), 7.77 (s, 1H, Im), 7.60 (s, 1H, NP), 7.58−7.46 (m, 4H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$, 294 K): 148.6 (CCN_{NP}), 142.8 (NCN_{NP}), 137.1 (CCC_{NP}), 135.3 (NCC_{NP}), 131.5 (CCC_{NP}), 130.8 (CCC_{NP}), 129.2 (CCC_{Ph}), 129.2 (CCC_{Ph}), 129.1 (NCC_{Ph}), 129. (CCC_{Ph}), 129.0 (CCC_{Ph}), 128.8 (CCC_{Ph}), 123.48 (CCC_{NP}), 121.6 (CCC_{NP}), 118.7 (NCC_{Im}), 112.60 (NCC_{Im}).

Synthesis of L^3Br. A 500 mg amount (2.03 mmol) of L^2H_2 was dissolved in glacial acetic acid (10 mL), and 0.2 mL of bromine was added. The mixture was stirred at room temperature for 15 h. The precipitate was filtered and redissolved in water. The suspension was made basic with sodium carbonate and extracted with dichloromethane. The organic layer was dried to give the pure product. Yield: 556 mg (86%). Mp: 204−206 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 8.87 (d, J = 4.3 Hz,1H, NP), 8.32 (d, J = 8.3 Hz, 1H, NP), 7.84 (s, 1H, Im), 7.82−7.78 (m, 3H, NP, Ph), 7.65 (dd, 1H, NP), 7.54−7.46 (m, 3H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$, 294 K): 148.6 (CCN_{NP}), 143.7 (NCN_{NP}), 142.1 (CCC_{NP}), 138.2 (NCC_{NP}), 137.6 (CCC_{NP}), 133.1 (CCC_{NP}), 130.7 (CCC_{Ph}), 130.0 (CCC_{Ph}), 129.4 (NCC_{Ph}), 129.3 (CCC_{Ph}), 129.2 (CCC_{Ph}), 129.1 (CCC_{Ph}), 127.6 (CCC_{NP}), 123.8 (CCC_{NP}), 122.8 (NCC_{Im}), 119.5 (NCC_{Im}).

Synthesis of 1. $[Cp^*IrCl_2]_2$ (44 mg, 0.06 mmol), NaOAc (28 mg, 0.34 mmol), and L^1H (33 mg, 0.12 mmol) were dissolved in dichloroethane (10 mL), and the mixture was refluxed for 4 h under nitrogen. The resulting orange-red suspension was filtered through a small bed of Celite. The filtrate was then concentrated under reduced pressure, followed by the addition of 15 mL of diethyl ether with stirring to induce precipitation. Repeated washings followed by prolonged drying under vacuum provided the cyclometalated compound **1** as a red solid. Crystals suitable for X-ray study were grown by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution of the compound. Yield: 66 mg (86%). Mp: >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 8.54 (s, 1H, NP), 7.82 (d, J = 7.75 Hz, 1H, Ph), 7.69 (d, J = 8.05 Hz, J = 10 Hz, 1H, NP), 7.63 (d, J = 7.15 Hz, 1H, Ph), 7.57 (d, J = 9.75 Hz, 1H, NP), 7.19 (s, 1H, Im), 7.11 (t, J = 7.3 Hz 1H, Ph), 7.0 (t, J = 7.42 Hz, 1H, Ph), 2.73 (s, 3H, CH_3NP), 2.67 (s, 3H, CH_3), 1.73 (s, 15H, CpMe_5). ^{13}C NMR (125 MHz, $CDCl_3$, 292 K): 159.2 (Ir−$C_{cyclometalated}$), 154.3 (NCN_{NP}), 146.6 (CCC_{NP}), 143.2 (NCC_{NP}), 139.0 (CCC_{NP}), 136.2 (CCC_{NP}), 129.7 (CCC_{NP}), 128.7 (CCC_{NP}), 126.8 (NCC_{NP}), 122.8 (CCC_{Ph}), 122.6 (CCC_{Ph}), 122.2 (CCC_{Ph}), 122.1 (CCC_{Ph}), 121.5 (CCC_{Ph}), 113.3 (NCC_{Im}), 104.1 (NCC_{Im}), 87.5 (*Cp*Me$_5$), 24.8(CH_3), 18.7(CH_3), 9.47 (CpMe_5). ESI-MS: m/z 600 $[M - Cl]^+$, where M = $Ir(L^1)Cp^*Cl$. Anal. Calcd for $C_{28}H_{29}N_3ClIr$: C, 52.89; H, 4.60; N, 6.61. Found: C, 52.47; H, 4.56; N, 6.45.

Synthesis of 2. A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), NaOAc (25 mg, 0.31 mmol), and L^2H_2 (27 mg, 0.11 mmol) were reacted by following a procedure similar to the synthesis of **1**. Compound **2** was isolated as a red crystalline solid. Crystals suitable for X-ray study were grown by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution of the compound. Yield: 60 mg (91%). Mp: >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 8.60 (d, J = 4.6 Hz, 1H, NP), 8.47 (d, J = 1.7 Hz, 1H, Im), 8.18 (dd, J = 7.85 Hz, J = 1.15 Hz, 1H, NP), 7.95 (s, 1H, NP), 7.94 (d, J = 8 Hz, 1H, Ph), 7.89 (d, J = 7.75 Hz, 1H, Ph), 7.71 (d, J = 1.8 Hz, 1H, Im), 7.51 (dd, J = 8.15 Hz, J = 4.25 Hz, 1H, NP), 7.06 (t, J = 7.17 Hz, 1H, Ph), 7.06 (t, J = 5.9 Hz, 1H, Ph), 1.42 (s, 15H,CpMe_5). ^{13}C NMR (125 MHz, $CDCl_3$, 292 K): 154.3 (Ir−$C_{cyclometalated}$), 152.1 (NCN_{NP}), 147.7 (NCC_{NP}), 143.4 (NCC_{NP}), 137.1 (NCC_{NP}), 134.1 (CCC_{NP}), 132.1 (CCC_{NP}), 130.7 (CCC_{NP}), 128.7 (NCC_{Ph}), 124.3 (CCC_{Ph}), 122.9 (CCC_{Ph}), 122.1 (CCC_{Ph}), 118.8(NCC_{Im}), 113.3 (NCC_{Im}), 88.0 (*Cp*Me$_5$), 8.8 (CpMe_5). ESI-MS: m/z 572 $[M - Cl]^+$, where M = $Ir(L^2H)Cp^*Cl$. Anal. Calcd for $C_{26}H_{25}N_3ClIr$: C, 51.38; H, 4.15; N, 6.91. Found: C, 51.70; H, 4.25; N, 6.72.

Synthesis of 3. A mixture of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol), NaOAc (25 mg, 0.31 mmol), and L^2H_2 (14 mg, 0.05 mmol) was reacted following a procedure similar to the synthesis of **1** for a period of 12 h. Compound **3** was isolated as a red crystalline solid. Crystals suitable for X-ray study were grown by slow vapor diffusion of diethyl ether into a saturated dichloromethane solution of the compound. Yield: 45 mg (91%). Mp: >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 292 K): δ 8.72 (d, J = 5.5 Hz, 1H, NP), 8.34 (dd, J = 5.5 Hz, J = 1.25 Hz, 1H, NP), 8.02 (dd, J = 8.07 Hz, J = 1.25 Hz, 1H, Ph), 8.00 (dd, J = 7.35 Hz, J = 1.25 Hz, 1H, Ph), 7.70 (s, 1H, Im), 7.40 (dd, J = 8.1 Hz, J = 4.6 Hz, 1H, NP), 7.40 (s, 1H, NP), 7.04 − 6.97 (m, 2H, Ph), 1.81 (s, 15H, CpMe_5), 1.40(s, 15H, CpMe_5). ^{13}C NMR (125 MHz, $CDCl_3$, 292 K): 155.9 (Ir−-$C_{cyclometalated}$), 154.2 (Ir−$C_{cyclometalated}$),146.1 (NCN_{NP}), 144.1 (NCC_{NP}), 137.2 (NCC_{NP}), 134.4 (NCC_{NP}), 132.4 (CCC_{NP}), 129.7 (CCC_{NP}), 128.8 (CCC_{NP}), 122.2 (CCC_{NP}), 126.2 (CCC_{Ph}), 124.4 (CCC_{Ph}), 122.8 (CCC_{Ph}), 121.2(CCC_{Ph}), 119.9-(CCC_{Ph}), 114.5(NCC_{Im}), 88.9 (*Cp*Me$_5$), 87.9 (*Cp*Me$_5$) 9.6 (CpMe_5), 8.9 (CpMe_5). ESI-MS: m/z 934 $[M - Cl]^+$, where M = $Ir_2(L^2)$-$Cp_2^*Cl_2$. Anal. Calcd for $C_{36}H_{39}N_3Cl_2Ir_2$: C, 44.57; H, 4.05; N, 4.33. Found: C, 44.37; H, 4.07; N, 4.27.

Conversion of 2 to 3. Compound **2** (40 mg, 0.065 mmol) was taken up in a 10 mL DCE solution, $[Cp^*IrCl_2]_2$ (26 mg, 0.033 mmol) and NaOAc (32 mg, 0.39 mmol) were added, and the mixture was refluxed for 12 h; after that a procedure similar to the synthesis of **1** was followed. Yield: 61 mg (90%).

Synthesis of 4. A THF solution (10 mL) of anhydrous $SnCl_2$ (15 mg, 0.082 mmol) was added dropwise to a dichloromethane solution (10 mL) of **1** (51 mg, 0.08 mmol), whereupon the initial yellow solution turned bright orange. The resultant solution was concentrated under vacuum, and 15 mL of petroleum ether was added with stirring to induce precipitation. Repeated washing followed by prolonged drying under vacuum provided an orange crystalline solid. Crystals suitable for X-ray study were grown by layering petroleum ether over a dichloromethane solution of the compound. Yield: 62 mg (93%). Mp: >250 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 292 K): δ 9.09 (s, 1H, NP), 8.20 (d, J = 9.15 Hz, 1H, NP), 8.0 (dd, J = 6.85 Hz, J = 2.45 Hz, 1H, Ph), 7.62 (dd, J = 6.42 Hz, J = 1.85 Hz, 1H, Ph), 7.54 (s, 1H, Im), 7.44 (d, J = 10.1 Hz, 1H, NP), 7.19−7.15 (m, 2H, Ph), 2.72 (s, 3H, CH_3NP), 2.70 (s, 3H, CH_3NP), 1.71 (s, 15H, CpMe_5). ^{13}C NMR (125 MHz, DMSO-d_6, 294 K): 159.9 (Ir−$C_{cyclometalated}$), 155.6 (NCN_{NP}), 147.3 (CCC_{NP}), 142.7 (NCC_{NP}), 138.9 (CCC_{NP}), 138.1 (CCC_{NP}), 129.5 (CCC_{NP}), 128.3 (CCC_{NP}), 126.8 (NCC_{NP}), 124.2 (CCC_{Ph}), 124.1 (CCC_{Ph}), 123.4 (CCC_{Ph}), 122.2 (CCC_{Ph}), 122.1 (CCC_{Ph}), 112.0 (NCC_{Im}), 105.1 (NCC_{Im}), 92.0 (*Cp*Me$_5$), 24.8 (CH_3), 18.5(CH_3), 9.9 (CpMe_5). ESI-MS: m/z 600 $[Ir(L^1)Cp^*]^+$. Anal. Calcd for $C_{28}H_{29}N_3Cl_3SnIr$: C, 40.72; H, 3.54; N, 5.09. Found: C, 40.31; H, 3.52; N, 5.11.

Synthesis of 5. A THF solution (10 mL) of anhydrous $SnCl_2$ (30 mg, 0.164 mmol) was added dropwise to a dichloromethane solution (10 mL) of **3** (78 mg, 0.08 mmol) following a procedure similar to the synthesis of **4**. Compound **5** was isolated as a red crystalline solid. Yield: 100 mg (93%). Mp: >250 °C dec. ^{1}H NMR (500 MHz, DMSO-d_6, 292 K): δ 8.68(d, J = 5.1 Hz, 1H, NP), 8.55 (s, 1H, Im), 8.41 (d, J = 7.75 Hz, 1H, Ph), 8.31 (d, J = 8.3 Hz, 1H, NP), 7.83 (d, J = 7.75 Hz, 1H, Ph), 7.70−7.65 (m, 1H, NP), 7.26 (t, J = 7.6 Hz, 1H, Ph), 7.15 (J = 8.3 Hz, 1H, NP), 7.13 (t, 1H, Ph), 2.00 (s, 15H, CpMe_5), 1.52 (s, 15H, CpMe_5).

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Synthesis of 6. $Pd(CH_3COO)_2$ (30 mg, 0.134 mmol), Na_2CO_3 (16 mg, 0.136 mmol), and L^2H_2 (33 mg, 0.13 mmol) were dissolved in acetronitrile (10 mL), and the mixture was refluxed for 6 h under nitrogen. The resulting yellow suspension was filtered through a small bed of Celite. The filtrate was concentrated under reduced pressure, followed by the addition of 15 mL of diethyl ether with stirring to induce precipitation. Repeated washing (3 × 10 mL) with diethyl ether followed by prolonged drying under vacuum provided the cyclometalated compound **6** as a yellow crystalline solid. Crystals suitable for X-ray study were grown by layering diethyl ether over a saturated dichloromethane solution of the compound. Yield: 61 mg (86%). Mp: >250 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 292 K): δ 8.79 (d, J = 4.2 Hz, 1H, NP), 8.07 (d, J = 7.6 Hz, 1H, NP), 7.89 (d, J = 1.8 Hz, 1H, Im), 7.69 (dd, J = 7.7 Hz, J = 4.6 Hz, 1H, NP), 7.30 (d, J = 1.95 Hz, 1H, Im), 7.24 (d, J = 8.25 Hz, 1H, Ph), 7.06 (d, J = 1.85 Hz, 1H, Im), 7.03 (d, J = 7.65 Hz, 1H, Ph), 6.78 (t, J = 7.4 Hz, 1H, Ph), 6.69 (t, J = 7.4 Hz, 1H, Ph), 3.15 (s, 3H, CH_3COO). ^{13}C NMR (125 MHz, $CDCl_3$, 294 K): 180.2 (Pd−$C_{cyclometalated}$), 149.3 (NCN_{NP}), 138.0 (CCC_{NP}), 134.7 (NCC_{NP}), 130.3 (CCC_{NP}), 130.2 (CCC_{NP}), 128.4 (CCC_{NP}), 126.3 (CCC_{NP}), 126.2 (NCC_{NP}), 123.9 (CCC_{Ph}), 123.7 (CCC_{Ph}), 122.6 (CCC_{Ph}), 122.5 (CCC_{Ph}), 122.5 (CCC_{Ph}), 119.8 (NCC_{Im}), 112.6 (NCC_{Im}), 119.8 (CH_3COO), 24.76 (CH_3COO). ESI-MS: m/z 391 $[Pd(L^2H)(CH_3CN)]^+$. Anal. Calcd for $C_{34}H_{26}N_6O_4Pd_2$: C, 52.81; H, 3.20; N, 10.27. Found: C, 52.63; H, 3.43; N, 10.22.

Synthesis of 7. $Pd_2(dba)_3{\cdot}CHCl_3$ (30 mg, 0.134 mmol) and L^3Br (33 mg, 0.136 mmol) were dissolved in dichloromethane (10 mL), and the mixture was stirred for 4 h under nitrogen. The resulting yellow suspension was filtered through a small bed of Celite. The filtrate was concentrated under reduced pressure, followed by the addition of 15 mL of diethyl ether with stirring to induce precipitation. Repeated washing followed by prolonged drying under vacuum provided cyclometalated compound 7 as a yellow solid. Crystals suitable for X-ray study were grown by layering diethyl ether over a dichloromethane solution of the compound. Yield: 50 mg (86%). Mp: 115−117 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 292 K): δ 8.75 (d, 1H, NP), 8.49 (d, 1H, J = 7.75, NP), 8.01 (d, J = 7.35 Hz, 1H, NP), 7.94 (q, 1H, NP), 7.78−7.74 (m, 1H, Ph), 7.72 (s, 1H, Im), 7.67 (dd, J = 7.45 Hz, 1H, Ph), 7.50 (t, J = 8.25 Hz, 1H, Ph), 7.46−7.42 (m, 2H, Ph). ^{13}C NMR (125 MHz, DMSO-d_6, 292 K): 153.1 (Pd−$C_{cyclometalated}$), 147.9 (NCN_{NP}), 143.3 (CCC_{NP}), 138.3 (NCC_{NP}), 135.4 (CCC_{NP}), 129.9 (CCC_{Ph}), 129.8 (CCC_{Ph}), 129.4(CCC_{Ph}), 129.7 (CCC_{Ph}), 128.8 (CCC_{Ph}), 128.7 (CCC_{Ph}), 126.1 (CCC_{NP}), 124.2 (CCC_{NP}), 122.5 (CCC_{NP}), 119.4 (CCC_{NP}), 115.7 (NCC_{Im}). ESI-MS: m/z 392 $[Pd(L^3)(CH_3CN)]^+$. Anal. Calcd for $C_{16}N_3H_{10}BrPd$: C, 44.76; H, 2.34; N, 9.79. Found: C, 44.36; H, 2.41; N, 9.67.

X-ray Data Collection and Refinement. Single-crystal X-ray structural studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,[24] and the data were corrected for absorption using the SADABS program.[25] The structures were solved and refined using the SHELX suite of programs,[26] while additional crystallographic calculations were performed for compound **1**, **2**, **4**, and **7** by the "SQUEEZE" option in PLATON.[27] The crystallographic figures have been generated using Diamond 3 software[28] (50% probability thermal ellipsoids). The hydrogen atoms were included in geometrically calculated positions in the final stages of the refinement and were refined according to the "riding model". Hydrogen atoms of the water molecule were not included in the structure of **7**. All non-hydrogen atoms, except C1, C4, and C5 in compound **3**, were refined with anisotropic thermal parameters. Anisotropic treatment of these three atoms resulted in nonpositive-definite displacement tensors and were therefore subjected to isotropic refinement. CCDC files 938956−938962 contain supplementary crystallographic data for compounds **1**−**7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Figures, a table, and CIF files giving crystallographic data, NMR spectra, and ESI-MS data of compounds and the pseudo-chair conformation of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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