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Rational Design of Ligand Precursors to Prepare Abnormal (Mesoionic) and Normal Carbene Complexes and Zwitterionic CX-Type Palladacycles (X = C, N)

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The preparation of a series of ligand precursors that feature imidazo[1,2-*a*]pyridine and amido functional groups is reported. The reactions between the new ligand precursors, pyridine, and palladium acetate in DMF afforded monodentate Pd^{II} abnormal (mesoionic) carbene complexes. An isomeric Pd^{II} normal carbene complex with a formally identical steric environment to that of the abnormal carbene counterpart was also prepared. The isomeric pairs were characterized by X-ray structural studies. Under different complexation conditions, in which $PdCl_2$ was employed as metal precursor, a zwitterionic CC-type palladacycle formed by the C–H activation at the *ortho*-*N*-phenyl and methylene carbon atoms was obtained. The use of a similar ligand precursor with an NH instead of an NMe group produced a zwitterionic palladalactam complex. In contrast to the previous work in the literature, owing to the rigidity of the fused heterocyclic ring, the palladalactam complex did not undergo intramolecular proton transfer through the coordinated N atom. Overall, we demonstrated that proper modification of the structures of ligand precursors and complexation conditions allowed us to obtain a full range of intriguing Pd^{II} complexes including normal and abnormal carbene complexes, and zwitterionic palladalactam and CC-type palladacycles by means of A–H bond (A = N, C) activations.

Introduction

Since the isolation and crystallographic characterization of the first free carbene by Arduengo et al.,[1] N-heterocyclic carbene (NHC) ligands have been extensively studied and proven to be highly versatile in a wide range of catalytic transformations.[2] Recently, it has been shown that imidazole-based NHC ligands could have an alternative binding mode through the C(4/5) atom instead of the common C(2) atom in the imidazolium ring.[3] Such "abnormal" (mesoionic) NHC ligands have been attracting attention,[4] because they are usually stronger electron donors than their normal counterparts[3a,5] and thus exhibited better catalytic activities in general,[5d,6] especially in reactions that involve the activation of unreactive bonds.[5d,6a,6f] Previously, we published the ligand precursor **1a**,**b** (Scheme 1) that bears amido and imidazole moieties, in which there were several sites that could undergo C–H cleavage to generate bidentate Pd complexes, including palladalactam **3a**, the five- and six-membered palladacycles **4a**,**b** and the six-membered palladacycle **5a**, which resulted from *N*-phenyl metalation (Scheme 2).[7] The formation of **4a** involved an interesting intramolecular proton-transfer mechanism from **3a**. Notably, the ligand precursor **1a**,**b** also consists of a C4 proton on the heterocyclic ring, which could deprotonate to form an abnormal carbene complex. Theoretical calculation, however, showed that the formation of an abnormal carbene complex derived from **1a** was energetically unfavorable. In this study, we redesigned ligand precursor **2**; the major difference from **1** is that it possesses an imidazo[1,2-*a*]pyridine moiety instead of an imidazole moiety. Also, the C5 position on the imidazole ring is blocked with an aryl group. Such modification in the structure results in a change of coordination activity, including the successful formation of abnormal carbene complexes. It is of great interest to achieve a Pd^{II} abnormal carbene complex with an amido functional group since Pd^{II} complexes with normal carbene analogues have been shown to be highly efficient in catalyzing classical and nonclassical C–C coupling reactions.[8] For comparative purposes, we designed and prepared **2′** as well. It was a potential ligand precursor for achieving an isomeric Pd^{II} normal carbene complex with a formally identical steric environment around the metal centers to the abnormal and normal carbene complexes. Interestingly, by varying the complexation conditions, a CC-type palladacycle formed by C–H activation at the *ortho*-*N*-phenyl and methylene carbon atoms was also obtained. Intriguingly, we found that the aforementioned intramolecular proton transfer was forbidden in the palladalactam complex derived from the new ligand precursor. Also it is note-

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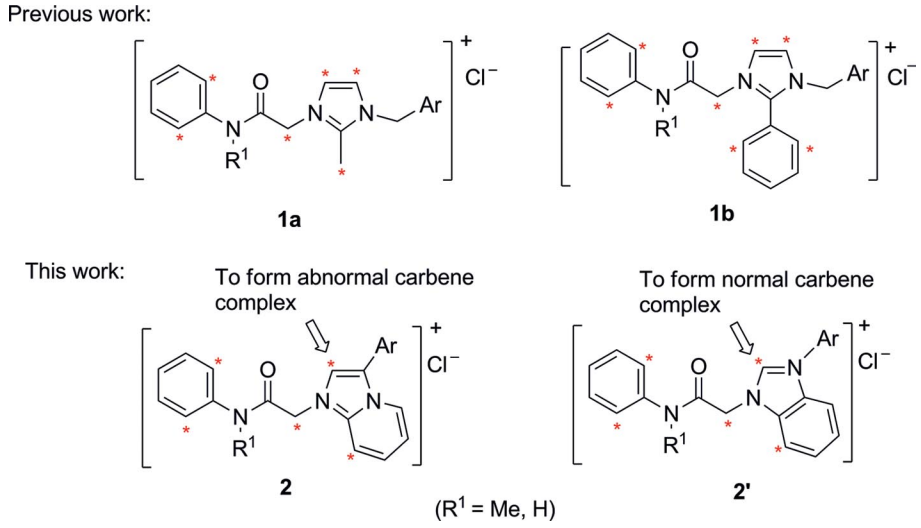
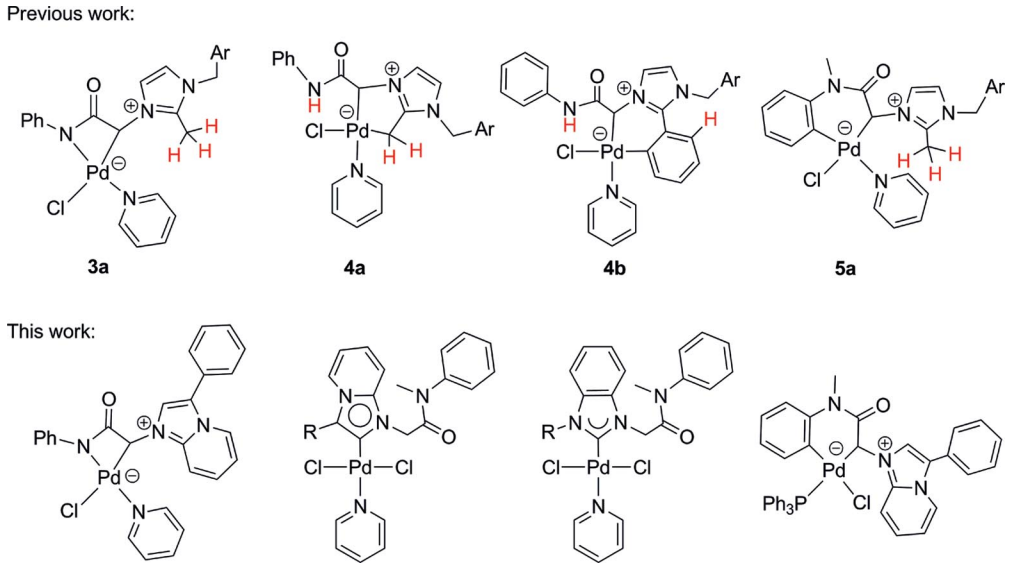


Scheme 1. Ligand precursors used in this work. Potential deprotonation sites are marked with asterisks.



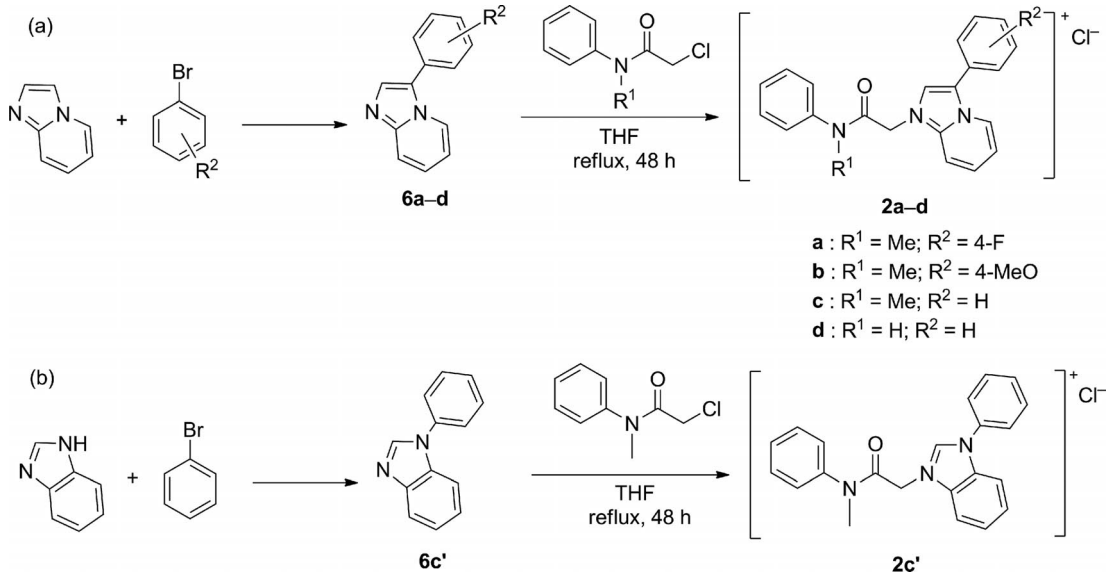
Scheme 2. Range of Pd^{II} complexes derived from ligand precursors **1**, **2**, and **2′**.

worthy to mention that the CC-type palladacycles and palladalactams are zwitterionic organometallates that feature anionic palladium centers.[9] Whereas zwitterionic cationic metal complexes are attracting growing interest for catalytic applications and are common in the literature,[9a,9b] anionic metal complexes are relatively rare, and most of them have been derived from phosphonium ylides or conjugated equivalents.[9c] The imidazolium precursors in Scheme 1 represent a new class of versatile ligand precursors for the synthesis of zwitterionic anionic palladacycles. As also shown in Scheme 2, since no non-zwitterionic connected Lewis structure can be drawn by resonance of the π electrons, the CC-type palladacycles and palladalactam complexes can be classified as "mesoionic" or "truly zwitterionic". The synthetic details and characterizations including single-crystal X-ray diffraction studies are presented.

Results and Discussion

Preparation of Ligand Precursors

Ligand precursors **2a**–**d** were prepared as shown in Scheme 3a. The intermediates **6a**–**d** were prepared by the regioselective Pd-catalyzed direct C–H arylation between imidazo[1,2-*a*]pyridine and aryl bromides.[10] Such a strategy allowed the easy tuning of the electronic property of the ligands; in particular, the coupled aryl/phenyl rings are the wingtip groups of the potentially formed abnormal carbene ligands.[11] Subsequent quaternization reactions of the imidazo[1,2-*a*]pyridine derivatives with 2-chloro-*N*-methyl-*N*-phenylacetamide or 2-chloro-*N*-phenylacetamide led to the formation of **2a**–**d** in pure form with 60–77% yields. The C*H* protons on the heteroaromatic rings in **2a**–

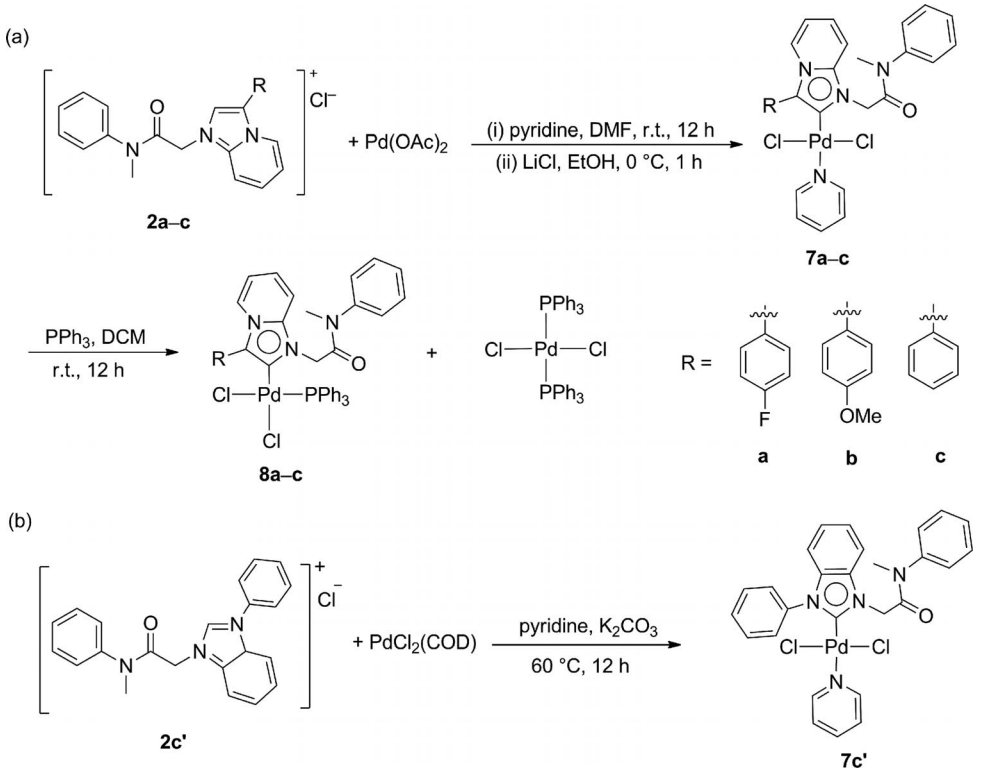


Scheme 3. Synthesis of ligand precursors.

d that deprotonate resonate at $\delta \approx 8.8$ ppm, which is similar to those in the related ligand precursors based on imidazo[1,2-*a*]pyridine.[11] Compounds **2a**–**c**, which bear *N*-methyl groups, are potential ligand precursors for the preparation of monodentate abnormal carbene complexes. For purposes of comparison, it is of interest to obtain the isomeric normal carbene complex. Thus, we also synthesized the ligand precursor **2c**′. The preparation was similar to that of **2c**. Instead of the imidazo[1,2-*a*]pyridine derivative **6c**, the benzoimidazole derivative **6c**′ was used in the quaternization reaction with 2-chloro-*N*-methyl-*N*-phenylacetamide (Scheme 3b). The NC*H*N proton that deprotonates resonates downfield at $\delta = 11.36$ ppm relative to those protons with signals at $\delta \approx 8.8$ ppm in **2a**–**c**.

Preparation of Pd^{II} Abnormal (Mesoionic) and Normal Carbene Complexes

Since compound **2a**–**c** contain several C–H sites that can undergo deprotonation, we explored different Pd^{II} precur-



Scheme 4. Synthesis of Pd^{II} abnormal and normal carbene complexes.

sors and complexation conditions to obtain novel Pd^{II} complexes. In view of the fact that the preparation of normal carbene Pd complexes by reaction of $Pd(OAc)_2$ with imidazolium salt was routinely employed, we stirred a mixture of the ligand precursors **2a**–**c**, pyridine, and $Pd(OAc)_2$ in DMF at ambient temperature with subsequent addition of LiCl to the solution, which gave the monodentate Pd^{II} abnormal carbene complexes **7a**–**c** in pure form (Scheme 4a). Successful formation of **7** was indicated by the absence of a proton signal at $\delta \approx 8.8$ ppm in its NMR spectrum with respect to that of the ligand precursors. These complexes were stable in air but decomposed readily in dichloromethane. To locate the carbene carbon signals in these complexes, we performed a heteronuclear multiple bond correlation (HMBC) experiment on **7b**, thereby confirming that the signal was at $\delta = 134.9$ ppm. Relevant *trans*-Pd^{II} abnormal carbene/pyridine complexes were reported by us previously.[11]

The isomeric normal carbene complex **7c′** was obtained by the reaction of the ligand precursor **2c′** with $[PdCl_2(cod)]$ (cod = cyclooctadiene) in the presence of base in pyridine (Scheme 4b). Similar *trans*-Pd^{II} carbene/pyridine complexes have been reported by others[2i,12] and us.[13] It is noteworthy that **7c** and **7c′** are an isomeric pair that share a formally identical steric environment around their metal centers.[11] The carbene signal in the normal carbene complex was observed at $\delta = 164.0$ ppm, which is more downfield to that at $\delta = 135.8$ ppm in the abnormal counterpart.

The pyridine ligands in complexes **7a**–**c** were easily substituted by PPh_3 to form complexes **8a**–**c**, which exhibited

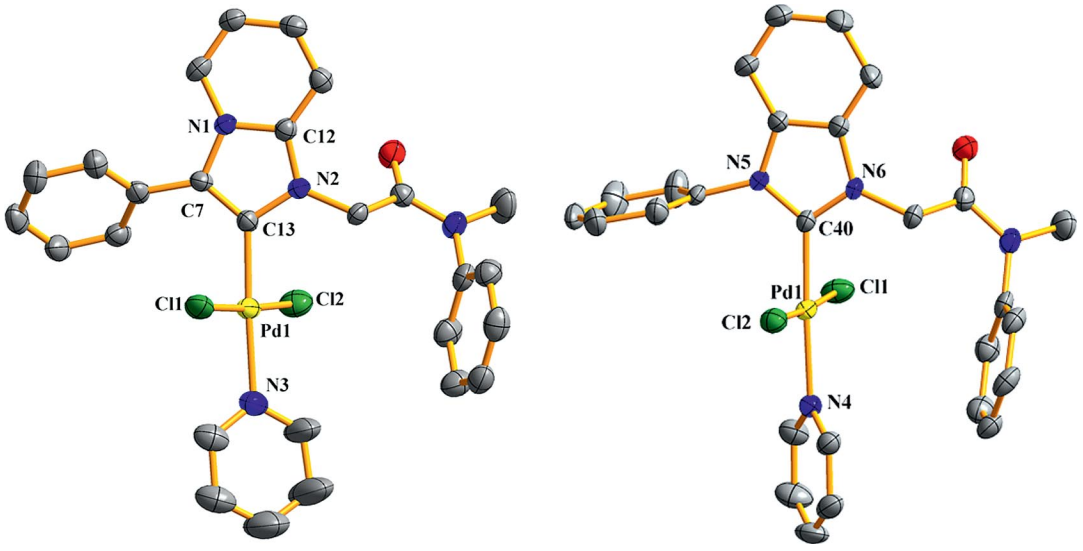


Figure 1. Molecular structures of **7c** (left) and **7c′** (right) with 50% probability ellipsoids for non-hydrogen atoms. Hydrogen atoms are omitted for clarity. Only one of the independent molecules in the structure of **7c′** is shown.

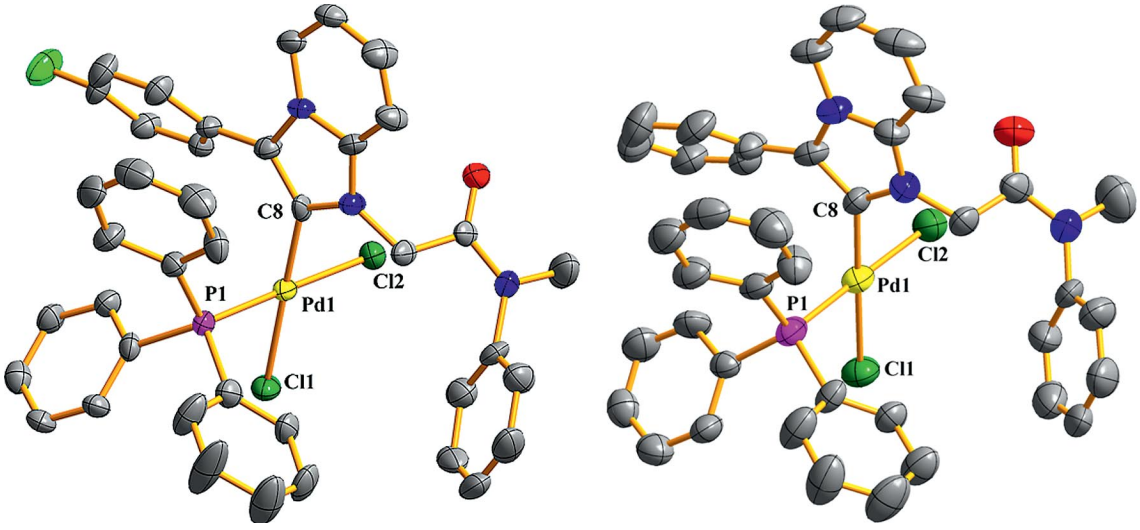


Figure 2. Molecular structures of **8a** (left) and **8c** (right) with 50% probability ellipsoids for non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

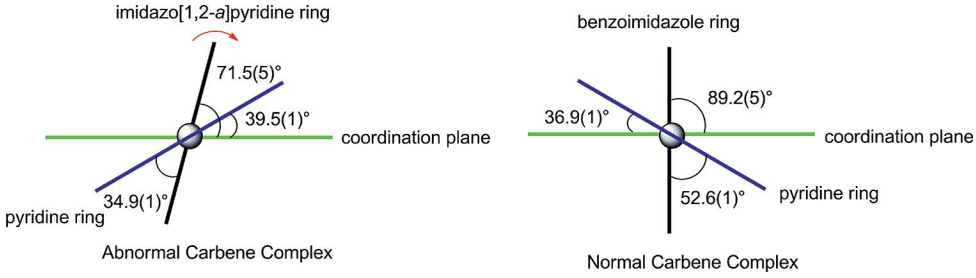


Figure 3. Schematic diagram viewing along the N–Pd–C axis illustrating the interplanar angles of least-squares mean planes in **7c** (left) and **7c′** (right).

phosphine resonances at $\delta \approx 28$ ppm. Notably, these complexes exhibit very poor solubility in common organic solvent, which prevented us from obtaining proper ^{13}C NMR spectra for **8a** and **8c**. Even though the solubility of **8b** was sufficient to obtain an adequate spectrum, the carbene signal was not observed, which was probably due to its coincidence with the phenyl signal at $\delta \approx 134$ ppm. Nevertheless, a *cis* disposition of the carbene and phosphine ligands in **8** was subsequently confirmed by X-ray diffraction studies. Examples of *cis*-PPh_3/carbene Pd^{II} complexes are known in the literature.[14]

Crystals of **7c**,**c′** and **8a**,**c** were grown, and their structures were established by X-ray diffraction studies (Figures 1 and 2, and Table S1 in the Supporting Information). Selected bond lengths and angles are provided in Tables 1 and 2. The Pd atoms in these structures adopt a distorted square-planar coordination geometry. The *trans* geometry of **7c**,**c′** was confirmed, whereas **8a**,**c** adopted a *cis* geometry. The structural analyses revealed that the Pd–C distance of abnormal carbene complex **7c** was slightly longer than that of its normal carbene counterpart [1.963(3) versus 1.951(3) Å]. The Pd–C bond length in **7c** is comparable to those of related *trans* pyridine/abnormal carbene complexes.[11] It is slightly shorter than the average bond length of 1.99(3) Å (seen in 41 crystallographically determined Pd complexes with abnormal carbene ligands).[4d] An important structural difference between the two structures is the orientation of the heterocyclic ring with respect to the coordination plane (which contains $PdCl_2CN$ atoms). The interplanar angle between the least-squares mean plane of the imidazo[1,2-*a*]pyridine ring and that of the coordination plane in **7c** is 71.5(5)°, whereas the benzoimidazole and the coordination plane in **7c′** are orthogonal to each other [89.2(5)°] (Figure 3).

Table 1. Selected bond lengths [Å] and angles [°] of **7c** and **7c′**.

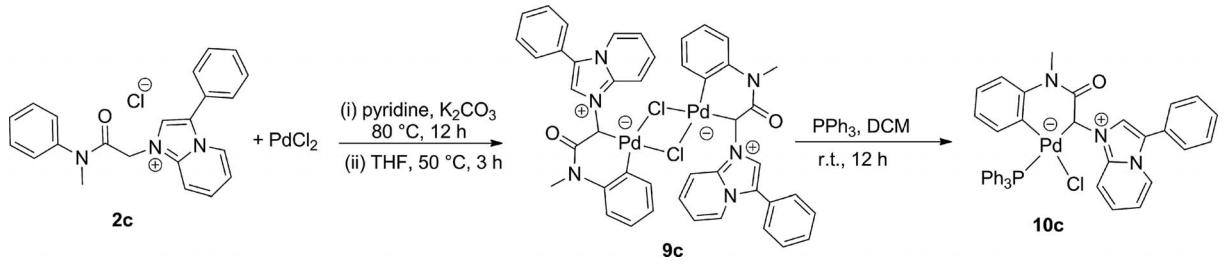
	7c		**7c′**
Pd1–C13	1.963(3)	Pd1–C40	1.951(3)
Pd1–N3	2.131(3)	Pd1–N4	2.103(2)
Pd1–Cl1	2.2999(9)	Pd1–C11	2.3059(9)
Pd1–Cl2	2.3052(10)	Pd1–C12	2.3136(8)
C13–Pd1–Cl1	86.65(9)	C40–Pd1–Cl1	88.31(9)
C13–Pd1–Cl2	89.85(9)	C40–Pd1–Cl2	87.44(9)
N3–Pd1–Cl1	91.48(9)	N4–Pd1–Cl1	92.36(7)
N3–Pd1–Cl2	92.12(9)	N4–Pd1–Cl2	91.91(7)
C13–Pd1 –N3	175.70(12)	C40–Pd1 –N4	177.21(10)
Cl1–Pd1–Cl2	176.22(3)	Cl1–Pd1–Cl2	175.71(3)

Table 2. Selected bond lengths [Å] and angles [°] of **8a**, **8c**, and **10c**.

	8a	**8c**		**10c**
Pd1–C	1.984(9)	2.001(8)	Pd1–C14	2.090(9)
Pd–Cl1	2.346(2)	2.353(3)	Pd1–C19	1.995(12)
Pd–Cl2	2.363(2)	2.361(3)	Pd1–Cl1	2.400(3)
Pd–P	2.243(2)	2.252(3)	Pd1–P1	2.328(3)
C–Pd–P	92.3(2)	92.2(2)	C14–Pd1–C19	79.8(5)
C–Pd–Cl2	87.5(2)	87.8(2)	C19–Pd1–P1	95.6(4)
Cl1–Pd–P	87.19(9)	87.80(9)	Cl1–Pd1–P1	88.62(11)
Cl1–Pd–Cl2	92.97(8)	92.25(9)	Cl1–Pd1–C14	97.5(3)
C–Pd –Cl1	178.6(2)	179.1(3)	C19–Pd1–Cl1	166.3(4)
P–Pd–Cl2	178.47(8)	178.59(10)	C14–Pd1–P1	171.6(4)

Synthesis of Zwitterionic CX-Type Palladacycles (X = C, N)

By applying different complexation conditions and heating of a mixture of **2c** with $PdCl_2$ in pyridine in the presence of K_2CO_3 as base, new dimeric Pd complex **9c** was obtained (Scheme 5) instead of the abnormal carbene complex. This complex is a zwitterionic CC-type palladacycle that exhibits an anionic palladium center. It was formed by the C–H activation at the *ortho*-*N*-phenyl and methylene carbon atoms, as indicated by the ^1H NMR spectrum of the reaction mixture displaying the characteristic methine proton resonance at $\delta = 5.94$ ppm, which is slightly downfield relative to the original methylene signal of the ligand precursor at $\delta = 5.29$ ppm. By changing the complexation conditions, an array of factors might contribute to such a drastic change in the outcome of the reaction. However, we believe that the difference in the solubility of the palladium precursors could play a crucial role. Previously, we successfully obtained the monomeric pyridine adduct **5a** by stirring the corresponding ligand precursor with $PdCl_2$ in pyridine at 80 °C with K_2CO_3 as base. However, in the case of **2c**, attempts to obtain an analogous monomeric adduct yielded an impure sample. Presumably, such a monomeric pyridine adduct was highly unstable, and partial decomposition that involved decoordination of the pyridine ligand occurred. Pleasingly, subsequent stirring of the crude solid in THF at 50 °C afforded the pyridine-free dimeric complex **9c** in pure form. Treatment of **9c** with PPh_3 in dichloromethane af-



Scheme 5. Formation of zwitterionic palladacycle by means of *ortho*-*N*-phenyl C–H activation.

forded the monomeric phosphine complex **10c**, which exhibits a phosphine resonance at $\delta \approx 25$ ppm. The presence of the CH proton signals at $\delta \approx 8.8$ ppm firmly excludes the possibility of **10c** and **9c** being abnormal carbene complexes. The resonance of the coordinated methine carbon atom in **10c** is observed at $\delta = 54.0$ ppm as a doublet with a coupling constant of 105.7 Hz, thus indicating that the phosphine ligand is in the *trans* disposition. The methine proton signal appears at $\delta = 5.98$ ppm, which is also slightly downfield relative to the methylene signal of its ligand precursor at $\delta = 5.29$ ppm. The deshielding of the coordinated CH resonances in **9c** and **10c** suggests a possible acidic character of the CH units. However, attempts to deprotonate these protons with a variety of bases resulted in the decomposition of the compounds. These complexes are stable in air and poorly dissolve in halogenated solvents. The poor solubility is attributable to the zwitterionic nature of these complexes. The structure of **10c** was successfully established by the X-ray diffraction analysis (Figure 4, Table 2). It features a Pd atom in distorted square-planar coordination geometry with the PPh_3 ligand *trans* to the methine carbon atom. The bite angle of the bidentate ligand is 79.8(5)°. The Pd–C bond *trans* to the P atom [2.090(9) Å] is longer than that *trans* to the Cl atom [1.995(12) Å], which is consistent with the higher *trans* influence of the phosphine ligand. Also, the Pd–P bond [2.328(3) Å] is longer than those of in **8a** and **8c** [2.243(2) and 2.252(3) Å, respectively], thus indicating the higher *trans* influence of the coordinated C atom.

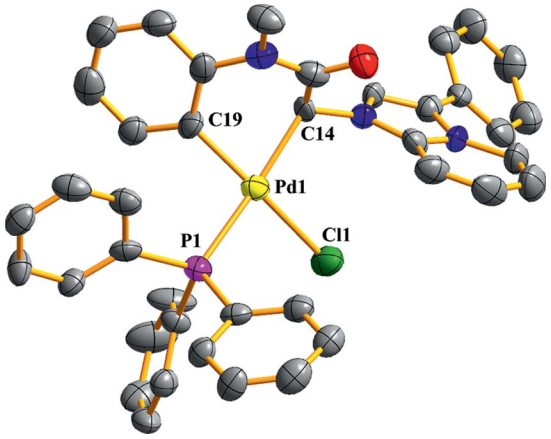
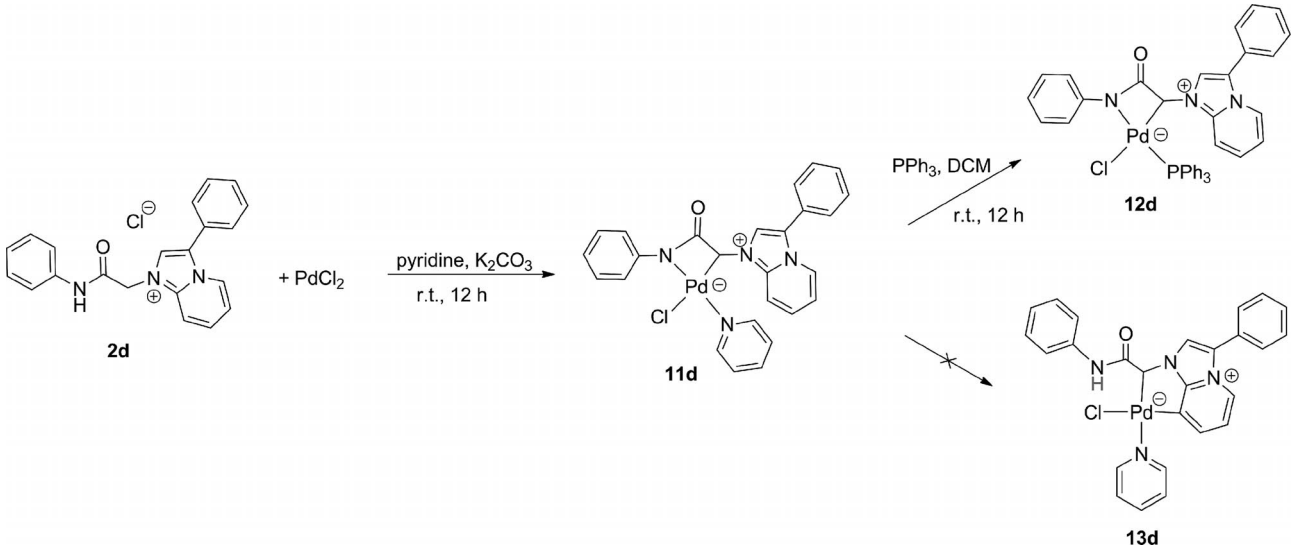


Figure 4. Molecular structures of **10c** with 35% probability ellipsoids for non-hydrogen atoms. Hydrogen atoms are omitted for clarity.

When using the ligand precursor **2d** that bears an NH instead of an NMe group on the amido moiety, the outcome of the complexation reaction was very different from that of **2c** (Scheme 6). Instead of the formation of a CC-type palladacycle with *N*-phenyl metalation such as **10c** or an abnormal carbene complex such as **7c**, the CN-type pal-



Scheme 6. Synthesis of zwitterionic palladalactam.

ladacycle, palladalactam complex **11d**, was obtained. This compound is similar to **3a** derived from ligand precursor **1a**.[7] Similar to **9c** and **10c**, compound **11d** is also a zwitterionic organometallic compound that features an anionic palladium ion. The methine signal is observed at δ = 4.92 ppm, which, unlike in the case of **9c** and **10c**, is upfield to the methylene signal in the ligand precursor **2d**. A substitution reaction of this complex with PPh_3 in dichloromethane afforded the zwitterionic phosphine complex **12d**, which shows a phosphine signal at δ = 29.0 ppm, similar to that at δ = 28.4 pm of a related compound.[7] The methine ^{13}C signal is observed as a singlet at δ = 39.0 ppm, which is consistent with the *cis* disposition of the PPh_3 ligand. The corresponding proton signal appears at δ = 4.87 ppm, which is also upfield to the methylene signal in the ligand precursor. It is noteworthy that the coordinated methine proton signals in the palladalactum compounds **3a**, **11d**, and **12d** that feature four-membered chelate rings appear at more upfield positions ($\delta \approx$ 4.6–4.9 ppm) with respect to the methylene signals of their ligand precursors, whereas the corresponding proton signals for the CC-type palladacycles **5a**, **9c**, and **10c**, which possess six-membered rings, are downfield shifted at $\delta \approx$ 5.6–6.0 ppm (see above), thereby reflecting the importance of the chelate ring size on the chemical shifts of the coordinated methine proton resonances. Interestingly, the coordinated N atom in **3a** could serve as an internal base to promote the hydrogen atom transfer of the methyl proton to the amido N atom to form the CC-type palladacycle **4a**.[7] Hydrogen atom transfer from an sp^2-carbon atom was also possible, thereby affording the six-membered palladacycle **4b** (see Scheme 2). However, in the case of **11d**, most likely on account of the rigidity of the fused heterocyclic ring, such internal proton transfer did not occur. Noteworthy, complex **11d** is soluble in common organic solvents. But like the aforementioned phosphine complex, **12d** exhibits only poor solubility in halogenated solvents, which could also be related to its zwitterionic nature.

Infrared Spectroscopy

The C=O stretching frequencies of the ligands in the normal and abnormal carbene complexes at approximately 1669 cm^{-1} are very similar, whereas those C=O bonds in the zwitterionic complexes stretch at lower frequencies and fall in a wider range of 1602–1621 cm^{-1}. Interestingly, the C=O stretching frequencies correlate well with their ^{13}C NMR spectroscopic chemical shifts (see the Supporting Information). For example, in **7b** and **11d**, the greater deshielding of the C=O nucleus in the latter complex (δ = 172.4 ppm in **11d** versus δ = 165.5 ppm in **7b**) reflects the reduced electron density about the C=O bond and hence a lower stretching frequency in **11d** (1602 versus 1668 cm^{-1} in **7b**).

Conclusion

On the basis of our previous works on the ligand precursors **1**, we designed and investigated the reactivity of the new ligand precursors **2a**–**c**, **2c′**, and **2d**. In contrast to **1**, complexation of **2a**–**c** with $Pd(OAc)_2$ led to the formation of the abnormal carbene Pd^{II} complex. An isomeric normal carbene Pd^{II} complex with a steric environment formally identical to that of the abnormal carbene counterpart was also obtained from the ligand precursor **2c′**. Instead of an abnormal carbene complex, a change in reaction conditions led to the formation of the zwitterionic CC-type palladacycle **10c** from the ligand precursor **2c**. Using the ligand precursor **2d**, the zwitterionic palladalactam complex **11d** was formed. Overall, we demonstrated that proper modification of the ligand precursors and complexation conditions allowed us to obtain a full range of intriguing Pd^{II} complexes including abnormal and normal carbene complexes, zwitterionic palladalactam and CC-type palladacycles by means of A–H bond (A = N, C) activations. Investigation of the catalytic properties of these new Pd^{II} complexes is ongoing in our laboratory. Intriguingly, the chiral character of **9c**, **10c**, **11d**, and **12d** owing to the formation of metal-anchored sp^3-carbon atoms could be explored for the development of pure chiral complexes, which might be applicable in asymmetric catalysis.

Experimental Section

General Considerations: All manipulations were performed under dry nitrogen by using standard Schlenk techniques. Solvents were dried by standard procedures. Starting chemicals were purchased from commercial sources and used as received. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13, 75.48, and 121.49 MHz, respectively, with a Bruker AV-300 spectrometer. Elemental analyses were carried out with a Thermo Flash 2000 CHN-O elemental analyzer. High-resolution mass spectroscopy (HRMS) was performed with a Finnigan/Thermo Quest MAT mass spectrometer at National Chung Hsing University (Taiwan). Infrared spectra were acquired with a Varian Cary 640 infrared spectrophotometer. Imidazo[1,2-*a*]pyridine was prepared according to a literature procedure.[15] Compounds **6a**–**d** and **6c′** were prepared according to literature procedures.[11] Since imidazolium derivatives **2a**–**d** and **2c′** are hygroscopic, HRMS was performed instead of elemental analyses. The purity of all the compounds was confirmed by their NMR spectra (see the Supporting Information).

Synthesis of 2a: A mixture of 3-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (2.00 g, 9.40 mmol) and 2-chloro-*N*-methyl-*N*-phenylacetamide (1.73 g, 9.40 mmol) in THF (30 mL) was placed in a Schlenk flask. The mixture was heated under reflux for 48 h. After cooling, the white solid was collected on a frit, washed with THF, and dried under vacuum. Yield: 2.80 g (77%). ^1H NMR ([D$_6$]DMSO): δ = 3.24 (s, 3 H, NCH_3), 5.26 (s, 2 H, NCH_2), 7.48–7.82 (m, 10 H, Ar *H*), 8.12 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.31–8.44 (m, 2 H, Ar *H*, imi *H*), 8.80 (d, $J_{H,H}$ = 6.0 Hz, 1 H, NC*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 37.9 (N*C*H$_3$), 49.5 (N*C*H$_2$), 113.0, 117.2 (d, $J_{C,F}$ = 21.8 Hz, *C*H), 118.4, 121.4, (d, $J_{C,F}$ = 3.7 Hz), 125.1, 125.2, 127.4, 128.1, 128.9, 130.4, 132.3 (d, $J_{C,F}$ = 9.0 Hz), 134.3, 140.6, 141.9, 163.5 (d, $J_{C,F}$ = 248 Hz), 164.7 (*C*=O) ppm. HRMS (ESI): calcd. for $C_{22}H_{19}ClFN_3O$ $[M - Cl]^+$ 360.1512; found 360.1517.

Synthesis of 2b: The compound was prepared by a procedure similar to that of **2a**. A mixture of 3-(4-methoxyphenyl)imidazo[1,2-*a*]-pyridine (2.00 g, 8.90 mmol) and 2-chloro-*N*-methyl-*N*-phenylacetamide (1.63 g, 8.90 mmol) was used. Yield: 2.0 g (60%). ^1H NMR

([D$_6$]DMSO): δ = 3.24 (s, 3 H, NCH_3), 3.86 (s, 3 H, OCH_3), 5.29 (s, 2 H, NCH_2), 7.20 (d, $J_{H,H}$ = 9.0 Hz, 2 H, Ar–*H*), 7.48–7.71 (m, 8 H, Ar *H*), 8.10 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.35 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.42 (s, 1 H, imi *H*), 8.77 (d, $J_{H,H}$ = 9.0 Hz, 1 H, NC*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 37.9 (NCH_3), 49.5 (NCH_2), 55.9 (O*C*H$_3$), 113.0, 115.5, 116.9, 118.3, 124.4, 126.1, 127.2, 128.1, 128.9, 130.4, 131.2, 134.0, 140.5, 141.9, 161.1 (*C*OCH$_3$), 164.7 (*C*=O) ppm. HRMS (ESI): calcd. for $C_{23}H_{22}ClN_3O_2$ [M – Cl]$^+$ 372.1712; found 372.1717.

Synthesis of 2c: The compound was prepared by a procedure similar to that of **2a**. A mixture of 3-phenylimidazo[1,2-*a*]pyridine (3.40 g, 17.0 mmol) and 2-chloro-*N*-methyl-*N*-phenylacetamide (3.21 g, 17.0 mmol) were used. Yield: 2.40 g (70%). ^1H NMR ([D$_6$]-DMSO): δ = 3.25 (s, 3 H, NCH_3), 5.29 (s, 2 H, NCH_2), 7.48–7.75 (m, 11 H, Ar *H*), 8.12 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.35 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.50 (s, 1 H, imi *H*), 8.85 (d, $J_{H,H}$ = 6.0 Hz, 1 H, NC*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 37.9 (N*C*H$_3$), 49.5 (N*C*H$_2$), 113.1, 118.4, 125.0, 126.1, 127.3, 128.2, 128.9, 129.5, 130.1, 130.4, 130.8, 134.2, 140.7, 141.9, 164.7 (*C*=O) ppm. HRMS (ESI): calcd. for $C_{22}H_{20}ClN_3O$ [M – Cl]$^+$ 342.1606; found 342.1610.

Synthesis of 2d: The compound was prepared by a procedure similar to that of **2a**. A mixture of 3-phenylimidazoimidazo[1,2-*a*]pyridine (3.20 g, 16.9 mmol) and 2-chloro-*N*-phenylacetamide (2.61 g, 16.9 mmol) were used. Yield: 4.40 g (74%). ^1H NMR ([D$_6$]DMSO): δ = 5.61 (s, 2 H, NCH_2), 7.05 (t, $J_{H,H}$ = 6.0 Hz, 1 H, Ar *H*), 7.30 (t, $J_{H,H}$ = 9.0 Hz, 2 H, Ar *H*), 7.53–7.75 (m, 8 H, Ar *H*), 8.09 (t, $J_{H,H}$ = 6.0 Hz, 1 H, NCCHC*H*), 8.39 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.58 (s, 1 H, imi *H*), 8.83 (d, $J_{H,H}$ = 6.0 Hz, 1 H, NC*H*), 11.17 (s, 1 H, N*H*) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 50.2 (N*C*H$_2$), 112.5, 118.4, 119.6, 124.2, 124.9, 125.1, 126.5, 127.5, 129.3, 129.7, 130.1, 130.9, 134.6, 139.0, 140.6, 164.1 (*C*=O) ppm. HRMS (ESI): calcd. for $C_{21}H_{18}ClN_3O$ [M – H]$^+$ 362.1060; found 362.1063.

Synthesis of 2c′: A mixture of 1-phenyl-1*H*-benzo[*d*]imidazole (0.870 g, 4.47 mmol) and 2-chloro-*N*-methyl-*N*-phenylacetamide (0.822 g, 4.47 mmol) in THF (30 mL) was placed in a Schlenk flask. The mixture was heated under reflux for 48 h. After cooling, the white solid was collected on a frit, washed with THF, and dried under vacuum. Yield: 0.500 g (30%). ^1H NMR ($CDCl_3$): δ = 3.32 (s, 3 H, NCH_3), 5.73 (s, 2 H, NCH_2), 7.25–7.79 (m, 14 H, Ar *H*), 11.29 (s, 1 H, NC*H*N) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 38.0 (N*C*H$_3$), 48.9 (N*C*H$_2$), 112.9, 113.5, 124.0, 124.8, 127.0, 127.5, 127.6, 128.1, 129.2, 130.1, 130.7, 130.8, 131.8, 132.9, 141.0, 144.0, 163.9 (*C*=O) ppm. HRMS (ESI): calcd. for $C_{22}H_{20}ClN_3O$ [M – Cl]$^+$ 342.1606; found 342.1604.

Synthesis of 7a: Dry DMF (10 mL) was added to a 20 mL Schlenk flask that contained $Pd(OAc)_2$ (0.226 g, 1.01 mmol), **2a** (0.4 g, 1.01 mmol), and pyridine (0.081 mL, 1.01 mmol). The mixture was stirred at ambient temperature for 12 h. The solvent was completely removed under vacuum, and a solution of LiCl (0.336 g, 8.08 mmol) in anhydrous ethanol (10 mL) was added to the brown residue, which was stirred vigorously for 30 min. The precipitate was washed with diethyl ether, filtered through a frit, and dried under vacuum. An air-stable yellow solid was obtained. Yield: 0.36 g (56%). M.p. 198.1–200.2 °C. $C_{27}H_{23}Cl_2FN_4OPd$ (615.81): calcd. C 52.66, H 3.76, N 9.10; found C 52.19, H 3.72, N 8.79. ^1H NMR ($CDCl_3$): δ = 3.32 (s, 3 H, NCH_3), 5.62 (s, 2 H, NCH_2), 7.01 (t, $J_{H,H}$ = 6.0 Hz, 1 H, Ar *H*), 7.19–7.75 (m, 12 H, Ar *H*), 7.99–8.04 (m, 2 H, Ar *H*), 8.16 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.90 (d, $J_{H,H}$ = 6.0 Hz, 2 H, py *H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 38.0 (N*C*H$_3$), 50.9 (N*C*H$_2$), 110.8, 115.1, 116.1 (d, $J_{C,F}$ = 21.8 Hz), 122.6, 124.2, 124.8, 125.0, 127.7, 127.8, 130.0, 132.6 (d, $J_{C,F}$ = 9.0 Hz), 135.9 (Pd–*C*), 137.8, 141.5, 142.4, 151.1, 162.9 (d, $J_{C,F}$ = 248 Hz), 165.5 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}.

Synthesis of 7b: The preparation was similar to that of **7a**. $Pd(OAc)_2$ (0.305 g, 1.36 mmol), **2b** (0.555 g, 1.36 mmol), pyridine (0.109 g, 0.136 mmol), and LiCl (0.114 g, 2.72 mmol) were used. A pale yellow solid was obtained. Yield: 0.270 g (55%). M.p. 263.2–264.5 °C. $C_{28}H_{26}Cl_2N_4O_2Pd$ (627.85): calcd. C 53.56, H 4.17, N 8.92; found C 53.85, H 4.19, N 8.99. ^1H NMR ($CDCl_3$): δ = 3.32 (s, 3 H, NCH_3), 3.85 (s, 3 H, OCH_3), 5.62 (s, 2 H, NCH_2), 6.69–7.07 (m, 3 H, Ar *H*), 7.26–7.41 (m, 6 H, Ar *H*), 7.55–7.64 (m, 3 H, Ar–*H*), 7.74 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 7.93 (d, $J_{H,H}$ = 9.0 Hz, 2 H, Ar *H*), 8.19 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.92 (d, $J_{H,H}$ = 6.0 Hz, 2 H, py *H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 38.0 (N*C*H$_3$), 50.9 (N*C*H$_2$), 55.3 (O*C*H$_3$), 110.7, 114.5, 114.8, 120.9, 122.8, 124.1, 125.9, 127.4, 127.8, 128.7, 130.0, 132.1, 134.9 (Pd–*C*), 137.6, 141.3, 142.5, 151.2, 159.9, 165.6 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 1668 (C=O) cm^{-1}.

Synthesis of 7c: The preparation was similar to that of **7a**. $Pd(OAc)_2$ (0.208 g, 0.930 mmol), **2c** (0.35 g, 0.93 mmol), pyridine (0.075 mL, 0.930 mmol), and LiCl (0.312 g, 7.45 mmol) were used. A pale yellow solid was obtained. Yield: 0.30 g (54%). M.p. 218.6–220.3 °C. $C_{27}H_{24}Cl_2N_4OPd$ (597.82): calcd. C 54.24, H 4.05, N 9.37; found C 53.76, H 3.92, N 8.90. ^1H NMR ($CDCl_3$): δ = 3.33 (s, 3 H, NCH_3), 5.65 (s, 2 H, NCH_2), 7.00 (t, $J_{H,H}$ = 6.0 Hz, 1 H, Ar *H*), 7.29–7.77 (m, 13 H, Ar *H*), 8.05 (d, $J_{H,H}$ = 6.0 Hz, 2 H, Ar *H*), 8.27 (d, $J_{H,H}$ = 6.0 Hz, 1 H, Ar *H*), 8.91 (d, $J_{H,H}$ = 6.0 Hz, 2 H, py *H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 38.0 (N*C*H$_3$), 51.0 (N*C*H$_2$), 110.7, 114.9, 122.9, 124.1, 125.0, 126.1, 127.6, 127.8, 128.7, 128.9, 129.0, 130.1, 130.6, 135.8 (Pd–*C*), 137.6, 141.5, 142.9, 151.2, 165.6 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}.

Synthesis of 7c′: In a 20 mL Schlenk flask, [$PdCl_2$(cod)] (0.088 g, 0.310 mmol), **2c′** (0.117 g, 0.310 mmol), and K_2CO_3 (0.171 g, 1.24 mmol) were dissolved in dry pyridine (10 mL) under nitrogen. The solution was stirred at 60 °C for 12 h. The solvent was completely removed under vacuum. The residue was redissolved in dichloromethane and washed with water. The organic phase was dried with anhydrous $MgSO_4$, and the solvents were evaporated to dryness under vacuum to give a solid. Diethyl ether was added, and the yellowish solid formed was collected on a frit and dried under vacuum. Yield: 0.083 g (45%). M.p. 250.1–250.5 °C. $C_{27}H_{24}Cl_2N_4OPd$ (597.82): calcd. C 54.24, H 4.05, N 9.37; found C 54.29, H 4.25, N 8.96. ^1H NMR ($CDCl_3$): δ = 3.35 (s, 3 H, NCH_3), 5.58 (s, 2 H, NCH_2), 7.28–7.63 (m, 14 H, Ar *H*), 7.75 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 7.94 (d, $J_{H,H}$ = 9.0 Hz, 2 H Ar *H*), 8.75 (d, $J_{H,H}$ = 3.0 Hz, 2 H Ar *H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 37.9 (N*C*H$_3$), 49.8 (N*C*H$_2$), 110.9, 111.6, 123.5, 123.8, 124.4, 127.7, 127.9, 128.7, 129.3, 129.5, 130.1, 135.2, 135.4, 136.9, 138.1, 142.6, 151.1, 164.0 (Pd–*C*), 165.6 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}.

Synthesis of 8a: In a 20 mL Schlenk flask, **7a** (0.20 g, 0.324 mmol) and PPh_3 (0.0851 g, 0.324 mmol) in dichloromethane (10 mL) were stirred at ambient temperature overnight. The mixture was filtered through silica, and the solvent was completely removed under vacuum. The residue was washed with THF in which the side product *trans*-[$PdCl_2(PPh_3)_3$] dissolved. The off-white solid was filtered through a frit and dried under vacuum. Yield: 0.14 g (55%). M.p. 234.6–235.4 °C. $C_{40}H_{33}Cl_2FN_3OPPd$ (799.00): calcd. C 60.13, H 4.16, N 5.26; found C 60.33, H 4.50, N 5.24. ^1H NMR ($CDCl_3$): δ = 3.08 (s, 3 H, NCH_3), 5.16–5.60 (m, 2 H, NCH_2), 7.05–7.72 (m, 27 H, Ar–*H*), 8.00 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 28.3 ppm. IR (KBr): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}.

Synthesis of 8b: The preparation was similar to that of **8a**. Complex **7b** (0.200 g, 0.318 mmol) and PPh_3 (0.0835 g, 0.318 mmol) were used. An air-stable yellow solid was obtained. Yield: 0.15 g (53%). M.p. 235.0–236.3 °C. $C_{41}H_{36}Cl_2N_3O_2PPd$ (811.03): calcd. C 60.72, H 4.47, N 5.18; found C 60.24, H 3.99, N 4.83. ^1H NMR ($CDCl_3$): δ = 3.05 (s, 3 H, NCH_3), 3.86 (s, 3 H, OCH_3), 5.23–5.41 (m, 2 H, NCH_2), 6.87–7.93 (m, 28 H, Ar *H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 37.8 (N*C*H$_3$), 51.1 (N*C*H$_2$), 55.5 (O*C*H$_3$), 110.2, 114.0, 115.2, 120.0, 122.6, 125.8 (d, $J_{P,C}$ = 6.8 Hz), 127.6 (d, $J_{P,C}$ = 10.5 Hz), 127.9, 128.1, 128.8, 129.8, 130.2, 130.5, 130.8, 131.6, 134.2 (d, $J_{P,C}$ = 11.3 Hz), 140.8, 141.9, 149.1, 165.0 (*C*=O) ppm; the Pd–*C* signal was not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 28.4 ppm. IR (KBr): $\tilde{\nu}$ = 1668 (C=O) cm^{-1}.

Synthesis of 8c: The preparation was similar to that of **8a**. Complex **7c** (0.200 g, 0.334 mmol) and PPh_3 (0.0870 g, 0.334 mmol) were used. An air-stable yellow solid was obtained. Yield: 0.11 g (67%). M.p. 228.7–229.5 °C. $C_{40}H_{34}Cl_2N_3OPPd$ (781.01): calcd. C 61.51, H 4.39, N 5.38; found C 61.90, H 3.96, N 5.17. ^1H NMR ($CDCl_3$): δ = 3.07 (s, 3 H, NCH_3), 5.19–5.60 (m, 2 H, NCH_2), 6.92–7.89 (m, 27 H, Ar *H*), 8.32 (br. s, 1 H, Ar *H*) ppm. $^{31}P\{^1H\}$ NMR ([D_6]DMSO): δ = 28.4 ppm. IR (KBr): $\tilde{\nu}$ = 1670 (C=O) cm^{-1}.

Synthesis of 9c: $PdCl_2$ (0.0600 g, 0.344 mmol), **2c** (0.13 g, 0.344 mmol), and K_2CO_3 (0.190 g, 1.38 mmol) were added to a 20 mL Schlenk flask and dissolved in dry pyridine (10 mL) under nitrogen. The solution was stirred at 80 °C overnight. The solvent was then completely removed under vacuum. The residue was re-dissolved in dichloromethane and washed with water. The organic phase was dried with anhydrous $MgSO_4$, and the solvents were evaporated to dryness under vacuum to give a solid. This solid was redissolved in THF, and the solution was stirred at 50 °C for 3 h. A yellow solid formed. It was collected on a frit, washed with diethyl ether, and dried under vacuum. Yield: 0.0636 g (90% based on **2c**). M.p. 226.8–227.4 °C. $C_{44}H_{36}Cl_2N_6O_2Pd_2$ (964.51): calcd. C 54.79, H 3.76, N 8.71; found C 54.57, H 4.05, N 8.30. ^1H NMR ([D_6]DMSO): 3.27 (s, 6 H, NCH_3), 5.94 (s, 2 H, PdC*H*), 6.88–7.00 (m, 6 H, Ar *H*), 7.36–8.01 (m, 18 H, Ar *H*), 8.49 (s, 2 H, imi *H*), 8.69 (d, d, $J_{H,H}$ = 3.0 Hz, 2 H, NC*H*) ppm. $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 33.3 (N*C*H$_3$), 47.6 (*C*HCO), 115.5, 116.7, 117.1, 123.2, 124.3, 124.7, 125.9, 126.0, 126.6, 129.2, 130.0, 130.2, 130.5, 137.8, 138.9, 144.6, 170.0 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 1621 (C=O) cm^{-1}.

Synthesis of 10c: In a 20 mL Schlenk flask, **9c** (0.500 g, 0.518 mmol) and PPh_3 (0.270 g, 1.04 mmol) in dichloromethane (10 mL) were stirred at ambient temperature overnight. An off-white solid was obtained. Yield: 0.550 g (71%). M.p. 209.3–209.6 °C. $C_{40}H_{33}ClN_3OPPd$ (744.55): calcd. C 64.53, H 4.47, N 5.64; found C 64.02, H 4.25, N 5.32. ^1H NMR ($CDCl_3$): δ = 3.40 (s, 3 H, NCH_3), 5.98 (d, $J_{H,H}$ = 12.0 Hz, 1 H, PdC*H*), 6.26–6.31 (m, 1 H, Ar *H*), 6.60–6.64 (m, 1 H, Ar *H*), 6.73–6.77 (m, 2 H, Ar *H*), 7.05 (t, $J_{H,H}$ = 6.0 Hz, 1 H, Ar *H*), 7.19–7.31 (m, 8 H, Ar *H*), 7.44–7.74 (m, 14 H, Ar *H*), 8.26 (d, $J_{H,H}$ = 6.0 Hz, 1 H, Ar *H*), 8.63 (s, 1 H, imi *H*) ppm. $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 33.3 (N*C*H$_3$), 54.0 (d, $J_{P,C}$ = 106 Hz, *C*HCO), 113.9, 115.6, 116.2, 122.3, 122.8, 124.1, 124.3, 125.9, 127.8 (d, $J_{P,C}$ = 10.5 Hz), 128.5, 129.3, 129.4, 129.8, 132.9 (d, $J_{P,C}$ = 36.9 Hz), 133.7 (d, $J_{P,C}$ = 19.6 Hz), 134.8 (d, $J_{P,C}$ = 12.0 Hz), 137.2, 139.4 (d, $J_{P,C}$ = 10.5 Hz), 144.0, 146.4 (d, $J_{P,C}$ = 7.5 Hz), 171. 8 (d, $J_{P,C}$ = 5.2 Hz, *C*O) ppm. $^{31}P\{^1H\}$ NMR ([D_6]DMSO): δ = 25.2 ppm. IR (KBr): $\tilde{\nu}$ = 1619 (C=O) cm^{-1}.

Synthesis of 11d: In a 20 mL Schlenk flask, $PdCl_2$ (0.200 g, 1.18 mmol), **2d** (0.430 g, 1.18 mmol), and K_2CO_3 (0.652 g, 4.72 mmol) were dissolved in dry pyridine (10 mL) under nitrogen. The solution was stirred at ambient temperature for 12 h. The solvent was completely removed under vacuum. The residue was redissolved in dichloromethane and washed with water. The organic phase was dried with anhydrous $MgSO_4$, and the solvents were evaporated to dryness under vacuum to give a solid. Diethyl ether was added, and the yellowish solid that had formed was collected on a frit, washed with more diethyl ether and methanol, and dried under vacuum. A yellowish solid was obtained. Yield: 0.26 g (45%). M.p. 211.6–212.1 °C. $C_{26}H_{21}ClN_4OPd$ (547.33): calcd. C 57.05, H 3.87, N 10.24; found C 57.55, H 4.23, N 9.89. ^1H NMR ($CDCl_3$): δ = 4.92 (s, 1 H, PdC*H*), 6.89 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 7.05 (t, $J_{H,H}$ = 9.0 Hz, 2 H, Ar *H*), 7.16–7.25 (m, 6 H, Ar *H*), 7.55–7.77 (m, 6 H, Ar *H*), 8.29–8.42 (m, 3 H, Ar *H*, imi *H*), 8.57 (d, $J_{H,H}$ = 3.0 Hz, 2 H, py *H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 31.0 (*C*HCO), 114.6, 116.9, 122.6, 124.2, 124.4, 124.7, 124.9, 125.4, 128.3, 129.3, 129.7, 130.6, 131.1, 137.3, 139.2, 144.4, 151.8, 172.4 (*C*=O) ppm. IR (KBr): $\tilde{\nu}$ = 1602 (C=O) cm^{-1}.

Synthesis of 12d: The preparation was similar to that of **8a**. Complex **11d** (0.160 g, 0.292 mmol) and PPh_3 (0.0760 g, 0.292 mmol) in dichloromethane (10 mL) were used. An air-stable yellow solid was obtained. Yield: 0.1 g (47%). M.p. 263.8–264.6 °C. $C_{39}H_{31}ClN_3OPPd$ (730.52): calcd. C 64.12, H 4.28, N 5.75; found C 63.92, H 4.55, N 5.08. ^1H NMR ([D_7]DMF): δ = 4.87 (d, $J_{H,H}$ = 3.0 Hz, 1 H, PdC*H*), 7.04 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 7.30–7.91 (m, 23 H, Ar *H*), 7.94 (t, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*), 8.17–8.20 (m, 2 H Ar *H*), 8.44 (d, $J_{H,H}$ = 9.0 Hz, 2 H, Ar *H*), 8.64 (m, 1 H, imi *H*), 8.86 (d, $J_{H,H}$ = 9.0 Hz, 1 H, Ar *H*) ppm. $^{13}C\{^1H\}$ NMR ([D_7]DMF): δ = 39.0 (Pd*C*H), 113.1, 117.4, 121.0, 123.9, 125.3 (d, $J_{P,C}$ = 15.0 Hz), 125.4, 126.3, 127.6, 128.2 (d, $J_{P,C}$ = 9.0 Hz), 129.1, 129.7, 130.2, 130.4, 132.2, 132.8, 134.6 (d, $J_{P,C}$ = 12.0 Hz), 139.9, 148.2, 173.0 (*C*=O) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 29.0 ppm. IR (KBr): $\tilde{\nu}$ = 1614 (C=O) cm^{-1}.

X-ray Diffraction Studies: Samples were collected at 150(2) K with a Bruker APEX II equipped with a CCD area detector and a graphite monochromator utilizing Mo-K_α radiation (λ = 0.71073 Å). The unit-cell parameters were obtained by least-squares refinement. Data collection and reduction were performed by using the Bruker APEX2 and SAINT software.[16] Absorption corrections were performed by using the SADABS program.[17] All the structures were solved by direct methods and refined by full-matrix least-squares methods against F^2 with the SHELXTL software package.[18] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions and refined with the use of a riding model. In the structure of **7c′**, there are two independent molecules in the asymmetric unit, and only one of them was used in the structural discussion. Crystallographic data are listed in Table 1. CCDC-935046 (**7c**), -935045 (**7c′**), -935047 (**8a**), -935048 (**3c**), and -935044 (**10c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic data for all the structures and NMR spectra for products.

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