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Syntheses and Structures of a Series of Acyclic Diaminocarbene Palladium(II) Complexes Derived from 3,4-Diaryl-1*H*-pyrrol-2,5-diimines and Bisisocyanide Palladium(II) Complexes

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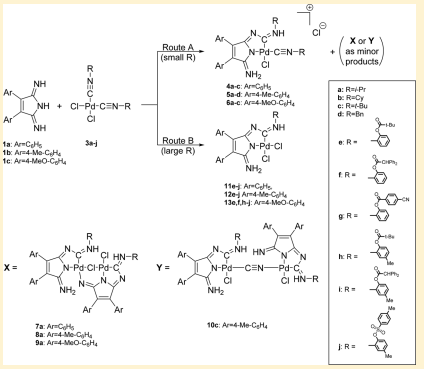
Supporting Information

ABSTRACT: Reactions of 3,4-diaryl-1*H*-pyrrol-2,5-diimines with various bisisocyanide palladium(II) complexes were studied. The coupling proceeds with one isocyanide ligand to accomplish the acyclic diaminocarbene complexes. The structure of generated diaminocarbene complexes depends on bulkiness of isocyanide ligand in the bisisocyanide complexes of palladium(II). The imino-group of 3,4-diaryl-1*H*-pyrrol-2,5-diimine reacts with one isocyanide ligand of *cis*-$[PdCl_2(CN{-}R)_2]$ (R = *i*-Pr, Cy, *t*-Bu, Bn), and the nitrogen atom of the pyrrole ring is coordinated to the palladium center as the second isocyanide ligand remains intact. In the case of *cis*-$[PdCl_2(CN{-}R)_2]$ (R = 2-acyloxyphenyl, 2-sulfonyloxyphenyl), one isocyanide ligand is displaced from the coordination sphere. Structural features of the prepared diaminocarbene complexes have been studied by molecular spectroscopy techniques, cyclic voltammetry, single-crystal X-ray diffraction, and DFT calculations. The photophysical properties of the obtained acyclic diaminocarbene complexes in solution mainly depend on the substituents in the 3,4-diaryl-1*H*-pyrrol-2,5-diimine moiety.

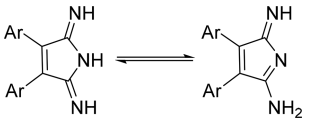


INTRODUCTION

The addition of N-nucleophiles to coordinated isocyanides is a facile synthetic pathway to acyclic diaminocarbene palladium(II) complexes, which attract attention as efficient catalysts and luminescent and bioactive compounds.[1,2] The metal center in this reaction not only activates the coordinated isonitriles toward the nucleophilic attack but also stabilizes acyclic diaminocarbenes (ADCs), which are unstable in free form. While sp^3-N-nucleophiles have been known to react in this fashion already for half a century,[3,4] exploration of reactivity of sp^2-N-nucleophiles toward coordinated isocyanides has been initiated a decade ago.[5,6] It is shown that the use of polynucleophiles leads to the formation of chelating ligands containing carbene moieties.[6−10]

The present work studies the reactions of polynucleophiles, namely, 3,4-diaryl-1*H*-pyrrol-2,5-diimines, with bisisocyanide palladium(II) complexes. It is well-known that imino and pyrrole nitrogen atoms in 3,4-diaryl-1*H*-pyrrol-2,5-diimines possess as nucleophilic centers. Moreover, based on computational studies, the equilibrium between imino and enamino forms is possible in solution (Scheme 1).[11,12] Therefore, these molecules may potentially react with isocyanide palladium(II) complexes in various modes. We reported a full study related to regioselectivity of the nucleophilic addition reaction, as well as the influence of steric and electronic effects of substituents in the nucleophiles and coordinated isocyanides on the structures and photophysical properties of diaminocarbene products.

Scheme 1. Tautomeric Forms of 3,4-Diaryl-1*H*-pyrrol-2,5-diimines



RESULTS AND DISCUSSION

Synthesis and Characterization of Complexes 4−6 and 11−13. 3,4-Diaryl-1*H*-pyrrol-2,5-diimines (aryl = phenyl (**1a**), 4-methylphenyl (**1b**), 4-methoxyphenyl (**1c**)) were synthesized from the appropriate arylacetonitriles according to the previously published method.[12−14]

Commercially available isocyanides RNC (R = isopropyl (**2a**), *tert*-butyl (**2b**), cyclohexyl (**2c**), benzyl (**2d**)) as well as isocyanides obtained in our research group (R = 2-(*tert*-butylcarbonyloxy)phenyl (**2e**), 2-

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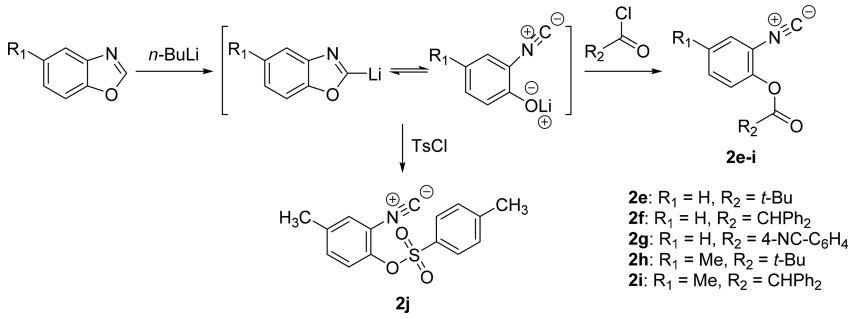
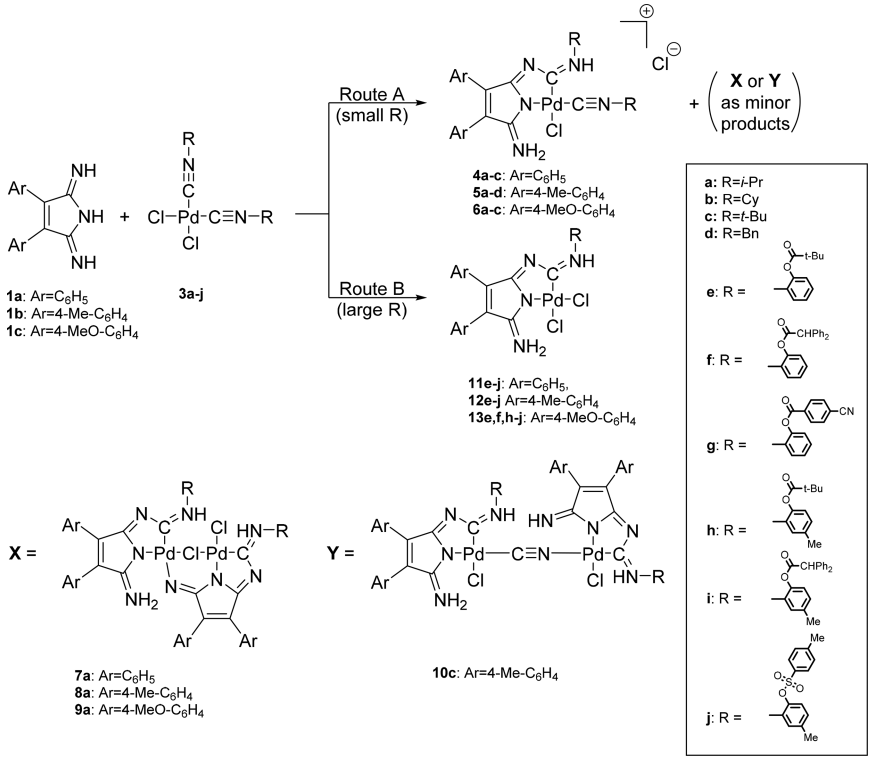
Scheme 2. Syntheses of Arylisocyanides 2e−j



Scheme 3. Reactions of 3,4-Diaryl-1*H*-pyrrol-2,5-diimines 1a−c and *cis*-[$PdCl_2(CN{-}R)_2$] 3a−j



(diphenylmethylcarbonyloxy)phenyl (**2f**), 2-(4-cyanophenylcarbonyloxy)phenyl (**2g**), 2-(*tert*-butylcarbonyloxy)-5-methylphenyl (**2h**), 2-(diphenylmethylcarbonyloxy)-5-methylphenyl (**2i**))[15−17] (Scheme 2) were used. In addition to 2-isocyanophenyl esters of carboxylic acids (**2e−i**), 2-isocyano-4-methylphenyl ester of *p*-toluenesulfonic acid (**2j**) was prepared using the same synthetic approach. This is the first example of the synthesis of 2-isocyanophenyl ethers of sulfonic acids by this method.

The bisisocyanide palladium(II) complexes *cis*-[$PdCl_2(CN{-}R)_2$] (R = isopropyl (**3a**), *tert*-butyl (**3b**), cyclohexyl (**3c**), benzyl (**3d**), 2-(*tert*-butylcarbonyloxy)phenyl (**3e**), 2-(diphenylmethylcarbonyloxy)phenyl (**3f**), 2-(4-cyanophenylcarbonyloxy)phenyl (**3g**), 2-(*tert*-butylcarbonyloxy)-5-methylphenyl (**3h**), 2-(diphenylmethylcarbonyloxy)-5-methylphenyl (**3i**), 5-methyl-2-(4-methylphenylsulfonyloxy)-phenyl (**3j**)) were prepared from isocyanides RNC **2a−j** and [$PdCl_2(CH_3CN)_2$] by the ligand exchange reaction.[4]

When a solution of bisisocyanide complex **3a−d** and 3,4-diaryl-1*H*-pyrrol-2,5-diimine **1a−c** in dichloromethane was stirred at room temperature for 2 h, chelate diaminocarbene complexes **4−6** were formed (Route A, Scheme 3). During the reaction, one isocyanide ligand in **3a−d** undergoes a nucleophilic attack by the imino group of **1a−c**, whereas the second remains intact. The imino nitrogen atom of **1** is attached to the carbon atom of the isocyanide group, whereas the nitrogen atom of the pyrrole ring coordinates to the metal center, thus closing the five-membered palladocycle. Monocarbene complexes were obtained as a result.

According to the previously reported DFT calculations,[12] the natural charges on the nitrogen atom of the pyrrole ring and on the nitrogen atom of the imino group in **1a−c** are −0.66 and −0.75, respectively, indicating that the sp^2-hybridized nitrogen atom of the imino group in **1a−c** is more nucleophilic than the pyrrole nitrogen atom. The observed reaction products are in agreement with these computations, since the coordinated isocyanides react selectively with the imino group. It is assumed that the reaction starts by attack of the nitrogen atom of the imino group to the carbon atom of the isocyanide group followed by the deprotonation and coordination of the pyrrole nitrogen

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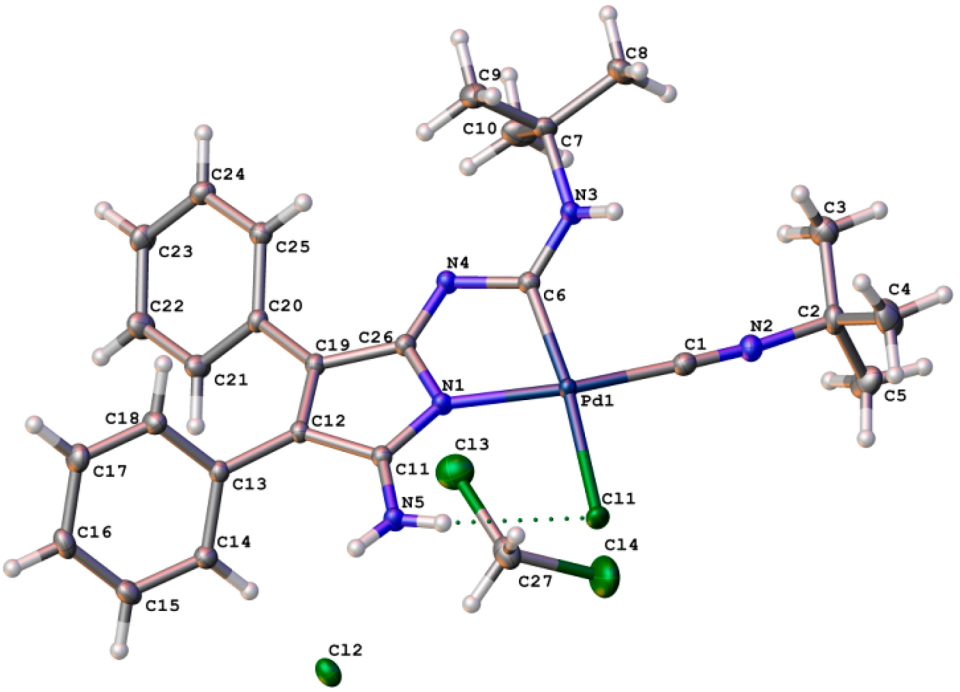

Figure 1. Molecular structure of **4c**·CH_2Cl_2.

atom to the palladium center accompanied by the ring closure to give five-membered palladocycle.

According to the ^{1}H NMR data, in some cases, along with the main products the side products have been observed. The reactions of **3a** with **1a**−**c** gave main products **4a**−**6a** together with minor side products **7a**−**9a** (Scheme 3). In **7a**−**9a**, the two palladium atoms are connected through a bridging chloride ligand and one of the 1*H*-pyrrol-2,5-diimine moieties. Another binuclear byproduct **10c** (Scheme 3) was detected in the reaction between **1b** and **3c**. In **10c**, the two palladium centers are linked together via the CN group resulting from the dissociation of the *tert*-butyl isocyanide ligand.

Single-crystal X-ray diffraction analyses were performed on complexes **4c**, **9a**, and **10c** after recrystallization from dichloromethane at room temperature.

4c·CH_2Cl_2 is crystallized in the triclinic space group $P\bar{1}$ (Figure 1). The palladium center is coordinated by the chelating diaminocarbene, *tert*-butyl isocyanide, and chloride ligands with a distorted square-planar geometry around the palladium center (the C6−Pd1−N1 angle in the five membered palladocycle is 77.86(5)°). The C6−N3 and C6−N4 bond lengths (1.302(2) and 1.396(2) Å, respectively) are not equal and are between the typical lengths for double (1.27 Å) and single (1.47 Å) carbon−nitrogen bonds.[18] The Pd1−C6 bond length (1.985(1) Å) is on the region of the lower boundary of the standard lengths interval of the single Pd−C bonds (1.98−2.13 Å),[19] which indicates an insignificant contribution of the back π-donation of electrons from the palladium atom to the carbene carbon atom. This is explained by the population of the C6 carbon atom p_π-orbital by electrons from the N3 and N4 atoms. The structure possesses the intramolecular (N5)H^N···Cl1 hydrogen bond (2.51(2) Å). The structure of **4c** optimized using DFT calculations is in agreement with the experimental XRD data (see the Supporting Information).

The structure of binuclear complex **9a** is shown in Figure 2. The compound is crystallized in the monoclinic space group

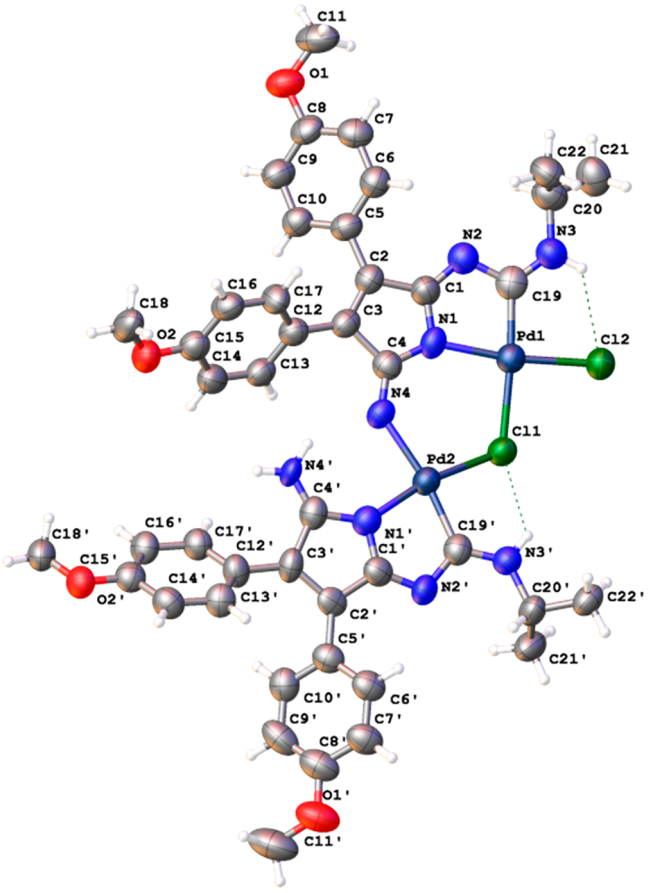

Figure 2. Molecular structure of **9a**.

$P2_1/c$. The Pd1 and Pd2 centers have distorted square planar geometry. The N1−Pd1−C19 and N1′−Pd2−C19′ angles are 79.8(5) and 77.5(4)°, respectively. The two palladium centers are linked together by the 3,4-di(4-methoxyphenyl)-1*H*-pyrrol-

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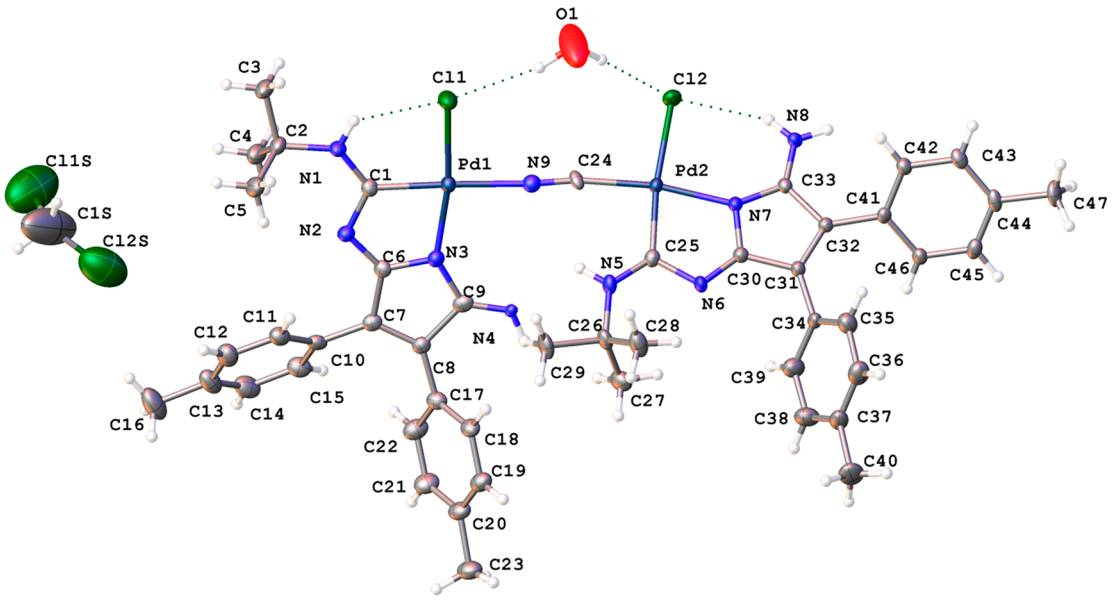

Figure 3. Molecular structure of **10c**·H_2O·0.5CH_2Cl_2.

2,5-diimine fragment and the bridging chloride ligand. The structure possesses the intramolecular N4···H4′A (2.27(2) Å), Cl2···H3 (2.50(2) Å), and Cl1···H3′ (2.50(2) Å) hydrogen bonds.

10c·H_2O·0.5CH_2Cl_2 crystallizes in the monoclinic $P2_1/c$ space group (Figure 3). The palladium centers exhibit the distorted square planar geometry. The Pd1 and Pd2 atoms are linked together via the CN group. The intramolecular Cl1···H(N1) and Cl2···H(N8) hydrogen bonds are 2.42(2) and 2.48(2) Å, respectively. The water molecule is linked to complex **10c** via two hydrogen bonds (Cl1···H(O1) (2.44(2) Å) and Cl2···H(O1) (2.41(2) Å)).

In contrast to the aforementioned reactions of **1a−c** with **3a−d**, the reactions with **3e−j** containing the bulky isocyanide ligands proceed via route B (Scheme 3) and afford **11−13**. One of the isocyanide ligands in **3e−j** undergoes nucleophilic attack of the imino group of **1a−c**, whereas the second isocyanide ligand leaves the metal coordination sphere. As the result, in the structures of **11−13**, the palladium center is bonded by one chelating diaminocarbene ligand and two chloride ligands.

The solid-state structure of **11j** was determined by X-ray crystallography (Figure 4). **11j** crystallizes from acetonitrile as a monosolvate in the monoclinic space group $P2_1/c$. The palladium center exhibits a distorted square planar geometry, with N1−Pd1−C17 angle of 77.9°. The value of Pd1−C17 bond length (1.958(2) Å) is shorter than the Pd−C bond length in **4c** (1.985(1) Å). As in **4c**, the C17−N3 bond (1.318(3) Å) is shorter than the C17−N2 bond (1.385(3) Å). The Pd1−Cl1 bond length (2.4008(6) Å) is larger than the Pd1−Cl2 bond length (2.3187(6) Å), which can be attributed to strong trans influence of the diaminocarbene ligand.[20] In the crystal structure of **11j**, intramolecular (Cl1···H4A (2.379(3) Å) and Cl2···H3 (2.413(3) Å)) hydrogen bonds are observed. The bond lengths and angles in the optimized structure of **11j** are comparable with the XRD data. (see the Supporting Information).

Thus, the reaction of **1** and **3** depends on the bulkiness of the isocyanide ligands. The relatively small size of R in **3a−d** favors reaction route A, allowing the formation of **4−6**. For

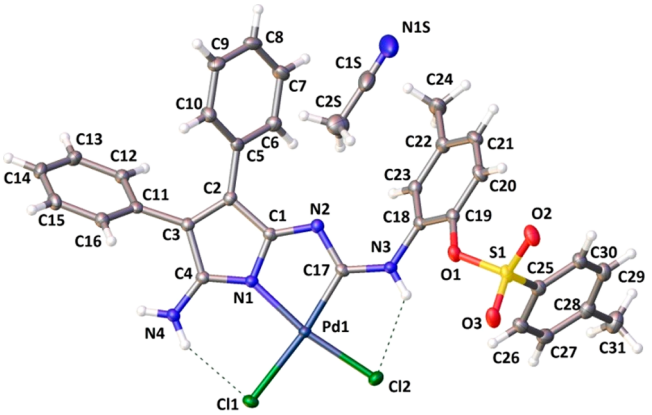

Figure 4. Molecular structure of **11j**·CH_3CN.

complexes **3e−j**, reaction route B becomes more favorable owing to the increased bulkiness of *o*-acyloxyphenyl substituents.

Optical Spectroscopy and Computational Studies. The absorption and fluorescence properties of the synthesized compounds **4−6** and **11−13** were evaluated by UV−vis absorption and emission spectroscopies at a concentration of $5{\cdot}10^{-5}$ M in chloroform (Table 1).

In order to identify the electronic transitions responsible for the absorption bands, TD−DFT studies of compounds **4c**, **11j**, and **12e** were undertaken (see Figure S55 and Tables S9−S11). The comparison of the calculated spectra with the experimental ones showed better match with the deprotonated forms [**4c**−HCl], [**11j**−H]$^-$, and [**12e**−H]$^-$ (see Figure S55). This confirms that the hydrogen of the iminium group has a high acidity in the solution. The absorption spectra of **4−6** display an intense absorption band in the range of 345−380 nm (see Figure S40). A significant redshift in comparison with the absorption spectra of **1a−c** (λ_{abs} at 278−311 nm)[12] can be explained by the extended π-conjugation due to the formation of the diaminocarbene moiety. The presence of the donor substituents at the phenyl rings of the 1*H*-pyrrol-2,5-diimine fragment leads to the redshift of the absorption band like in

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Table 1. Absorption and Emission Properties of 4−6 and 11−13 in Chloroform Solution ($c = 5 \times 10^{-5}$ M)

compd	λ_{abs} (nm)	$\varepsilon \times 10^{-4}$ (M^{-1} cm^{-1})	λ_{em} (nm)	Stokes shift (nm)
4a	350	2.0	468	118
4b	355	1.8	502	147
4c	359	1.4	491	132
5a	362	1.6	516	154
5b	366	1.5	480	114
5c	370	1.4	515	145
5d	361	1.7	496	135
6a	397	0.9	510	113
6b	381	1.0	551	170
6c	388	1.5	555	167
11e	378	1.4	494	116
11f	385	1.2	494	109
11g	370	1.2	495	125
11h	360	0.9	496	136
11i	398	1.1	492	94
11j	400	1.2	438	38
12e	394	1.2	515	121
12f	397	1.6	521	124
12g	401	1.5	530	129
12h	377	1.4	512	135
12i	410	1.3	517	107
12j	404	1.5	450	46
13e	413	1.4	550	137
13f	415	1.1	554	139
13h	400	1.3	553	153
13i	420	1.9	553	133
13j	407	1.5	560	153

1a−c.[12] In general, the greater the electron-donating ability of a substituent toward the conjugated backbone, the more effective the conjugation and intramolecular charge transfer. For [**4c**−HCl], the important one-electron transitions are from HOMO to LUMO (f = 0.063) and from HOMO−3 to LUMO (f = 0.20) (see Table S9). The schematic representations of the molecular orbitals for [**4c**−HCl], and their energies were exhibited in Table S4.

Compounds **11−13** showed the maximum absorbance at larger wavelengths (λ_{abs} at 360−420 nm) (see Figure S41) compared to those of **1a−c** (λ_{abs} at 278−311 nm).[12] These bands have a more complex structure, being broader and having shoulders, which may be due to the participation of the conjugated 2-acyloxyphenyl and 2-sulfonyloxyphenyl fragments in electronic $\pi-\pi^*$ transitions. As in the case of **4−6**, the peak maxima of the compounds with the donor substituents at the phenyl rings of the 1*H*-pyrrol-2,5-diimine fragment are obviously red-shifted. Both groups of complexes (**4−6** and **11−13**) possess weak absorption in the visible range (at ca. 500 nm for **4−6** and ca. 550 nm for **11−13**), which can be tentatively attributed to forbidden transitions involving metal d-orbitals. For [**11j**−H]$^-$, the important one-electron transitions are from HOMO−5 (f = 0.20) and HOMO−7 (f = 0.10) to LUMO (see Table S10). For [**12e**−H]$^-$, the one-electron transitions with the largest oscillator strength are from HOMO−5 (f = 0.18 and 0.15) and HOMO−7 (f = 0.052) to LUMO (see Table S11). Also, the schematic representations of the molecular orbitals are exhibited in Tables S6 and S8.

Complexes **4−6** and **11−13** exhibit fluorescence in the visible range of 468−560 nm (Table 1). Similar to absorption, donor substituents at the phenyl rings of the pyrroldiimine fragment generally cause red shift of the fluorescence emission bands. Fluorescence lifetimes and quantum yields were measured for **4−6b**, **12e**, and **12j**. The fluorescence lifetimes are in the range 8.6−19.8 ns. All tested compounds with the exception of **6b** possess low luminescence. The fluorescence quantum yields for **4b**, **5b**, **12e**, and **12j** vary in the range of 1−4%. A relatively high quantum yield (Φ_f = 27%) is observed for compound **6b** bearing the electron-donating methoxy groups in the 3,4-diaryl-1*H*-pyrrol-2,5-diimine fragment.

Electrochemical Reduction. The electrochemical behaviors of complexes **4a**, **5a**, **5b**, and **11e** were analyzed by cyclic voltammetry in acetonitrile at different scan rates from 0.1 to 1 $V \cdot s^{-1}$. At the cathodic scan, all compounds exhibit irreversible electrochemical response with well-defined reduction peaks (see Figure S42 and Table S1). The products of the electrochemical reduction (palladium(0) complexes) are electrooxidizable, producing a small anodic wave (E_p from 0.2 to 0.43 V) during the subsequent anodic scan.

CONCLUSION

The presence of steric hindrance triggers different pathways in the reactions of 3,4-diaryl-1*H*-pyrrol-2,5-diimines with *cis*-[$PdCl_2(CN-R)_2$]. In particular, the steric effect of isocyanide ligands is an important factor inducing the formation of the expected (**4−6**) and unexpected (**11−13**) products. The reaction of 3,4-diaryl-1*H*-pyrrol-2,5-diimines and [$PdCl_2(CNR)_2$], where R = *i*-Pr, Cy, *t*-Bu, Bn, leads to the formation of complexes **4−6**. In the case of bisisocyanide complexes with the bulky isocyanide ligands, such as 2-acyloxyphenyl isocyanides and 2-tosyloxyphenyl isocyanides, one isocyanide ligand leaves the metal coordination sphere; as a result, compounds **11−13** were formed. The insertion of donor substituents into pyrrole ring leads to the red shift of the absorption band in the UV−vis spectra. TD-DFT calculations allowed the assignment of the absorption bands in the visible region as predominantly intraligand transitions with a small metal-to-ligand charge transfer contribution.

EXPERIMENTAL SECTION

General Considerations. All solvents were dried and purified by conventional methods and were freshly distilled under argon shortly before use. Other reagents were used without further purification. FTIR spectra were recorded on Shimadzu FTIR-8400S (4000−400 cm^{-1}) and IRAffinity-1S (4000−300 cm^{-1}) spectrometers using KBr pellets. ^{1}H NMR measurements were performed on a Bruker-DPX 400 instrument at ambient temperature. Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source using MeOH as the solvent. The instrument was operated in both positive and negative ion modes using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI$^+$−MS) or 3500 V (ESI$^-$−MS) and the capillary exit at ± (70−150) V. The nebulizer gas flow was 0.4 bar and drying gas flow 4.0 L/min. The absorption spectra were recorded on a Perkin−Elmer precision spectrophotometer Lambda 1050. The emission spectra, excitation spectra, and measurements of the lifetimes of excited states were measured on a modular spectrofluorimeter Fluorolog-3 (Horiba Jobin Yvon). Fluorescence lifetime measurements are based on time-correlated single photon counting (TCSPC). Device also includes an integrating sphere Quanta-φ with fiber optics which enables direct measurement of quantum yields of luminescence. Cyclic voltammetry experiments were performed in acetonitrile at room temperature under argon, in a three-electrode cell using an Autolab potentiostat (PGSTAT 20). Tetrabutylammonium tetrafluoroborate ($TBABF_4$) used as the supporting electrolyte for the electrochemical investigations was prepared from $NaBF_4$ (Acros), and

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n-Bu_4NHSO_4 (Acros), recrystallized from ethyl acetate−hexane (both from Acros), and dried at 60 °C. The reference electrode was a saturated calomel electrode (SCE-Tacussel), which was separated from the solution by a bridge compartment filled with the same solvent/supporting electrolyte ($TBABF_4$) solution (0.1 M) as in the cell. The counterelectrode was a 1 cm length platinum wire (Goodfellow). A homemade glassy carbon electrode (1 mm diameter; Goodfellow) was used as the working electrode.

Complexes 4−6. 3,4-Diaryl-1*H*-pyrrol-2,5-diimine (**1a−c**) (0.1 mmol) was dissolved in dichloromethane (2 mL) and added to the solution of *cis*-[$PtCl_2(CNR)_2$] (**3a−d**) (0.1 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 2 h. Dichloromethane was evaporated under reduced pressure. Residue was washed by acetone and recrystallized from chloroform.

4a. Yield 84%, orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.64 (s, 1H, NCNH), 10.62 (s, 1H, NH), 10.14 (s, 1H, NH), 7.30−7.60 (m, 10H, Ph), 4.99 (br, 1H, CH), 3.98 (br, 1H, CH), 1.56 (br, 6H, *i*-Pr), 1.33 (br, 6H, *i*-Pr). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.3, 182.7, 171.4, 141.4, 140.2, 130.7, 130.2, 130.1, 129.7, 129.6, 129.2, 128.6, 128.5, 128.0, 52.0, 50.3, 22.3, 21.6. HRMS (ESI$^+$), *m*/*z*: 526.1011 [M − Cl]$^+$. $C_{24}H_{27}N_5ClPd$ Calcd *m*/*z*: 526.0990. IR spectrum (KBr, selected bands, cm^{-1}): 3400 w, ν(N−H), 3156, 3050 s, ν(C_{Ar}−H), 2980, 2932 s, ν(C−H), 2237 s, ν(C≡N), 1683 m, ν(C═N) 1554 s, ν(N−C═N). Anal. Calcd for $C_{24}H_{27}N_5Cl_2Pd\cdot CHCl_3$: C 44.01; H 4.14; N 10.27. Found: C 44.13; H 4.21; N 10.34.

4b. Yield 84%, orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.57 (s, 1H, NCNH), 11.12 (s, 1H, NH), 10.11 (s, 1H, NH), 7.30−7.55 (m, 10H, Ph), 4.57 (br, 1H, CHNH), 3.61 (br, 1H, CHNC), 2.15−2.35 (m, 2H, CH_{2Cy}), 1.70−2.00 (m, 6H, CH_{2Cy}), 1.20−1.70 (m, 12H, CH_{2Cy}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.2, 182.6, 171.3, 141.2, 140.0, 130.6, 130.2, 130.1, 129.7, 129.6, 129.2, 128.5, 128.4, 128.1, 59.5, 55.5, 31.4, 31.4, 25.3, 24.8, 24.2, 22.7. HRMS (ESI$^+$), *m*/*z*: 606.1667 [M − Cl]$^+$. $C_{30}H_{35}N_5ClPd$, Calcd *m*/*z*: 606.1616. IR spectrum (KBr, selected bands, cm^{-1}): 3415 w, ν(N−H), 3172, 3066 m, ν (C−H_{Ar}), 2935, 2856 s, ν(C−H), 2236 s, ν(C≡N), 1684 m, ν(C═N) 1554 s, ν(N−C═N). Anal. Calcd for $C_{30}H_{35}N_5Cl_2Pd\cdot CHCl_3$: C 48.84; H 4.76; N 9.19. Found: C 48.89; H 4.81; N 9.27.

4c. Yield 75%, orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.50 (s, 1H, NCNH), 10.91 (s, 1H, NH), 10.20 (s, 1H, NH), 7.30−7.50 (m, 10H, Ph), 1.65 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 192.6, 183.4, 171.8, 140.8, 139.6, 130.6, 130.2, 130.0, 129.9, 129.9, 129.1, 128.6, 128.5, 128.0, 59.6, 57.7, 29.8, 29.5. HRMS (ESI$^+$), *m*/*z*: 554.1351 [M − Cl]$^+$. $C_{26}H_{31}N_5ClPd$, Calcd *m*/*z*: 554.1303. IR spectrum (KBr, selected bands, cm^{-1}): 3400 w, ν(N−H), 3220, 3050 m, ν(C_{Ar}−H), 2982, 2930 s, ν(C−H), 2224 s, ν(C≡N), 1681 m, ν(C═N) 1538 s, ν(N−C═N). Anal. Calcd for $C_{26}H_{31}N_5Cl_2Pd\cdot CHCl_3$: C 45.66; H 4.54; N 9.86. Found: C 46.07; H 4.60; N 10.02.

5a. Yield 80%, red-orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.84 (s, 1H, NCNH), 10.17 (s, 1H, NH), 9.65 (s, 1H, NH), 7.43 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.31 (m, 4H, Ar), 7.16 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 5.00 (dsept, 1H, $^3J_{HH}$ = 6.4 Hz, $^3J_{HH}$ = 6.4 Hz, C*H*(CH_3)$_2$), 4.18 (sept, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*(CH_3)$_2$), 2.43 (s, 3H, Me), 2.38 (s, 3H, Me), 1.56 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH(C*H*$_3$)$_2$), 1.36 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.2, 182.9, 171.6, 141.0, 140.7, 140.4, 139.5, 130.4, 130.0, 129.5, 129.3, 129.2, 126.4, 125.2, 52.0, 50.3, 22.3, 21.6, 21.6, 21.5. HRMS (ESI$^+$), *m*/*z*: 554.1313 [M − Cl]$^+$. $C_{26}H_{31}N_5ClPd$ Calcd *m*/*z*: 554.1303. IR spectrum (KBr, selected bands, cm^{-1}): 3423 s, ν(N−H), 3226 s, ν(C_{Ar}−H), 2925 s, ν(C−H), 2224 s, ν(C≡N), 1718 s, ν(C═N), 1526 s, ν(N−C═N). Anal. Calcd for $C_{26}H_{31}N_5Cl_2Pd\cdot CHCl_3$: C 45.66; H 4.54; N 9.86. Found: C 46.01; H 4.58; N 9.92.

5b. Yield 90%, red crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.42 (s, 1H, NCNH), 11.19 (s, 1H, NH), 10.07 (s, 1H, NH), 7.41 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.34 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.27 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.13 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 4.56 (s, 1H, C*H*NH), 3.49 (s, 1H, CHNC), 2.40 (s, 3H, Me), 2.37 (s, 3H, Me), 2.20−2.30 (m, 2H, CH_{2Cy}), 1.80−2.00 (m, 6H, CH_{2Cy}), 1.20−1.70 (m, 12H, CH_{2Cy}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.5, 182.9, 171.4, 140.7, 140.5, 140.4, 139.2, 130.3, 130.1, 129.7, 129.1, 126.6, 125.3, 59.3, 55.4, 31.5, 31.3, 25.4, 24.8, 24.7, 22.9, 21.6, 21.5. HRMS (ESI$^+$), *m*/*z*: 634.1954 [M − Cl]$^+$. $C_{32}H_{39}ClN_5Pd$, Calcd *m*/*z*: 634.1929. IR spectrum (KBr, selected bands, cm^{-1}): 3427 s, ν(N−H), 3142 s, ν(C_{Ar}−H), 2934, 2856 s, ν(C−H), 2232 s, ν(C≡N), 1680 s, ν(C═N), 1556 s, ν(N−C═N). Anal. Calcd for $C_{32}H_{39}Cl_2N_5Pd\cdot CHCl_3$: C 50.15; H 5.10; N 8.86. Found: C 50.21; H 5.19; N 8.99.

5c. Yield 70%, red crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.87 (s, 1H, NCNH), 9.91 (s, 1H, NH), 9.25 (s, 1H, NH), 7.47 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.35 (d, 4H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.23 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.14 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 2.46 (s, 3H, Me), 2.38 (s, 3H, Me), 1.59 (s, 9H, *t*-Bu), 1.55 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 194.5, 187.3, 177.9, 140.0, 139.5, 139.2, 138.3, 130.2, 130.1, 129.9, 129.7, 125.9, 125.1, 59.6, 57.7, 25.4, 22.9, 21.5, 21.5. HRMS (ESI$^+$), *m*/*z*: 582.1647 [M − Cl]$^+$. $C_{28}H_{35}ClN_5Pd$, Calcd *m*/*z*: 582.1616. IR spectrum (KBr, selected bands, cm^{-1}): 3420 s, ν(N−H), 3260 s, ν(C_{Ar}−H), 2965, 2925 s, ν(C−H), 2230 s, ν(C≡N), 1723 s, ν(C═N). Anal. Calcd for $C_{28}H_{35}Cl_2N_5Pd\cdot CHCl_3$: C 47.18; H 4.91; N 9.49. Found: C 47.27; H 5.04; N 9.61.

5d. Yield 88%, orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.04 (s, 1H, NCNH), 10.22 (s, 1H, NH), 7.59 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.44 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.40 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.28−7.38 (m, 8H, Ar), 7.23 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.15 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 5.30−5.35 (m, 2H, CH_2), 5.18−5.23 (m, 2H, CH_2), 2.45 (s, 3H, Me), 2.40 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 194.0, 183.6, 172.2, 141.4, 140.0, 139.8, 139.6, 136.5, 130.8, 130.1, 129.9, 129.9, 129.3, 129.1, 129.0, 128.8, 128.5, 128.1, 127.8, 127.3, 125.9, 125.0, 51.1, 49.9, 21.6, 21.6. HRMS (ESI$^+$), *m*/*z*: 650.1370 [M − Cl]$^+$. $C_{34}H_{31}N_5ClPd$ Calcd *m*/*z*: 650.1303. IR spectrum (KBr, selected bands, cm^{-1}): 3181 s, ν(C_{Ar}−H), 2916 s, ν(C−H), 2250 s, ν(C≡N), 1683 s, ν(C═N), 1574, 1541 s, ν(N−C═N). Anal. Calcd for $C_{34}H_{31}N_5Cl_2Pd\cdot CHCl_3$: C 52.13; H 4.00; N 8.69. Found: C 52.22; H 4.08; N 8.73.

6a. Yield 85%, red crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.59 (s, 1H, NCNH), 10.29 (s, 1H, NH), 10.08 (s, 1H, NH), 7.51 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 7.40 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.01 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ar), 6.86 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 4.90−5.00 (m, 1H, C*H*NH), 4.05−4.15 (m, 1H, CHNC), 3.88 (s, 3H, OMe), 3.84 (s, 3H, OMe), 1.56 (br, 6H, CH(C*H*$_3$)$_2$), 1.33 (br, 6H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.2, 183.3, 171.9, 161.3, 161.1, 138.8, 138.3, 131.8, 131.3, 121.8, 120.5, 115.3, 114.0, 55.5, 55.4, 51.9, 50.3, 22.3, 21.6. HRMS (ESI$^+$), *m*/*z*: 586.1227 [M − Cl]$^+$. $C_{26}H_{31}N_5O_2ClPd$ Calcd *m*/*z*: 586.1201. IR spectrum (KBr, selected bands, cm^{-1}): 3397 s, ν(N−H), 3165 s, ν(C_{Ar}−H), 2974 s, ν(C−H), 2236 s, ν(C≡N), 1683 s, ν(C═N), 1554 s, ν(N−C═N). Anal. Calcd for $C_{26}H_{31}N_5O_2Cl_2Pd\cdot CHCl_3$: C 43.69; H 4.34; N 9.43. Found: C 43.72; H 4.38; N 9.48.

6b. Yield 85%, red-orange crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.53 (s, 1H, NCNH), 10.36 (s, 1H, NH), 10.09 (s, 1H, NH), 7.53 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 7.40 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 7.01 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 6.85 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 4.53−4.67 (m, 1H, C*H*NH), 4.00−4.10 (m, 1H, CHNC), 3.89 (s, 3H, OMe), 3.76 (s, 3H, OMe), 2.20−2.40 (m, 2H, CH_{2Cy}), 1.73−2.00 (m, 6H, CH_{2Cy}), 1.20−1.70 (m, 12H, CH_{2Cy}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.3, 183.1, 171.9, 161.3, 161.2, 138.6, 138.1, 131.8, 131.2, 121.8, 120.4, 115.3, 114.0, 63.8, 59.5, 55.5, 55.4, 31.5, 31.4, 25.4, 24.8, 24.7, 22.7. HRMS (ESI$^+$), *m*/*z*: 666.1909 [M − Cl]$^+$. $C_{32}H_{39}N_5O_2ClPd$, Calcd *m*/*z*: 666.1827. IR spectrum (KBr, selected bands, cm^{-1}): 3433 w, ν(N−H), 3152 s, ν(C−H_{Ar}), 2934, 2856 s, ν(C−H), 2245 s, ν(C≡N), 1690 m, ν(C═N) 1541 s, ν(N−C═N). Anal. Calcd for $C_{32}H_{39}N_5O_2Cl_2Pd\cdot CHCl_3$: C 48.20; H 4.90; N 8.52. Found: C 48.27; H 4.96; N 8.69.

6c. Yield 80%, brown crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.15 (s, 1H, NCNH) 10.72 (s, 1H, NH), 10.13 (s, 1H, NH), 7.46 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 7.42 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 6.96 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 6.83 (d, 2H, $^3J_{HH}$ = 8.8 Hz, Ar), 3.85 (s, 3H, OMe), 3.83 (s, 3H, OMe), 1.66 (s, 9H, *t*-Bu), 1.42 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 192.6, 184.2, 172.4, 161.4,

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161.4, 138.3, 138.0, 131.7, 130.9, 121.6, 120.3, 115.8, 114.0, 59.3, 55.6, 55.4, 55.3, 30.0, 29.5. HRMS (ESI$^+$), m/z: 614.1577 [M − Cl]$^+$. $C_{28}H_{35}N_5O_2ClPd$, Calcd m/z: 614.1514. IR spectrum (KBr, selected bands, cm^{-1}): 3402 s, ν(N−H), 3154 s, ν(C$_{Ar}$−H), 2971 s, ν(C−H), 2226 s, ν(C≡N), 1683 s, ν(C=N), 1549 s, ν(N−C=N). Anal. Calcd for $C_{28}H_{35}N_5O_2Cl_2Pd{\cdot}CHCl_3$: C 45.22; H 4.71; N 9.09. Found: C 45.31; H 4.79; N 9.14.

Complexes 11−13. 3,4-Diaryl-1*H*-pyrrol-2,5-diimine (0.1 mmol) was dissolved in acetonitrile (2 mL) and added to the solution of *cis*-[$PdCl_2(CNR)_2$] (0.1 mmol) in acetonitrile (2 mL). The reaction mixture was left overnight at room temperature. The precipitated solid was filtered.

11e. Yield 55%, red crystals. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.25 (s, 1H, NCNH), 10.91 (s, 1H, NH), 8.99 (d, 1H, $^3J_{HH}$ = 9.2 Hz, Ar), 7.50−7.60 (m, 5H, Ph), 7.30−7.50 (m, 4H, Ar), 7.25 (t, 2H, $^3J_{HH}$ = 7.6 Hz, Ar), 7.16 (t, 1H, $^3J_{HH}$ = 8.8 Hz, Ar), 7.11 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ar), 7.06 (s, 1H, NH), 1.43 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 194.5, 186.3, 176.7, 172.4, 143.4, 140.4, 140.3, 130.9, 130.7, 130.2, 130.2, 129.2, 129.1, 129.0, 128.5, 128.4, 128.1, 126.5, 125.8, 122.6, 39.6, 27.3. HRMS (ESI$^-$), m/z: 625.0395 [M − H]$^-$. $C_{28}H_{25}Cl_2N_4O_2Pd$, Calcd m/z: 625.0389. IR spectrum (KBr, selected bands, cm^{-1}): 3396 s, ν(N−H), 3176, 3044 s, ν(C$_{Ar}$−H), 2980 s, ν(C−H), 1757 s, ν(C=O), 1678 s, ν(C=N), 1526 s, ν(N−C=N). Anal. Calcd for $C_{28}H_{26}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 53.87; H 4.37; N 10.47. Found: C 53.85; H 4.36; N 10.40.

11f. Yield 49%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.44 (s, 1H, NCN*H*), 10.94 (s, 1H, NH), 7.76 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.45−7.60 (m, 12H, Ar), 7.36 (t, $^3J_{HH}$ = 7.6 Hz, 5H, Ar), 7.17−7.21 (m, 2H, Ar), 7.10−7.15 (m, 2H, Ar), 6.90 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar), 5.61 (s, 1H, C*H*Ph$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 192.9, 187.2, 172.8, 169.9, 161.4, 161.3, 142.5, 138.1, 137.7, 131.9, 131.2, 129.0, 129.0, 128.9, 128.8, 128.4, 127.5, 125.8, 124.6, 122.1, 121.3, 120.5, 115.6, 113.8, 56.6. HRMS (ESI$^-$), m/z: 735.0551 [M − H]$^-$. $C_{37}H_{27}Cl_2N_4O_2Pd$, Calcd m/z: 735.0546. IR spectrum (KBr, selected bands, cm^{-1}): 3406 w, ν(N−H), 3164, 3052, 3029 s, ν(C−H$_{Ar}$), 1764 s, ν(C=O), 1676 m, ν(C=N) 1534 s, ν(N−C=N). Anal. Calcd for $C_{37}H_{28}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 60.13; H 4.01; N 8.99. Found: C 60.14; H 4.00; N 8.92.

11g. Yield 42%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.68 (s, 1H, NCN*H*), 10.99 (s, 1H, NH), 8.42 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 8.27 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.83 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.50−7.60 (m, 5H, Ph), 7.40−7.45 (m, 5H, Ph), 7.33 (t, $^3J_{HH}$ = 8.0 Hz, 3H, Ar). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 193.9, 186.5, 170.1, 162.8, 146.0, 142.3, 140.2, 132.7, 132.5, 131.8, 131.3, 131.1, 131.0, 130.3, 130.1, 130.0, 129.9, 129.0, 129.0, 128.8, 128.6, 126.6, 125.6, 122.9, 117.5. HRMS (ESI$^-$), m/z: 670.0068 [M − H]$^-$. $C_{31}H_{20}Cl_2N_5O_2Pd$, 670.0029. IR spectrum (KBr, selected bands, cm^{-1}): 3530, 3425 m, ν(N−H), 3055 m, ν(C$_{Ar}$−H), 2986 m, ν(C−H), 2229 w, ν(C≡N), 1746 s, ν(C=O), 1678 s, ν(C=N), 1583 m, ν(C=N), 1534 s, ν(N−C=N). Anal. Calcd for $C_{31}H_{21}Cl_2N_5O_2Pd{\cdot}CH_3CN$: C 55.52; H 3.39; N 11.77. Found: C 55.50; H 3.38; N 11.71.

11h. Yield 54%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.29 (s, 1H, NCN*H*), 10.88 (s, 1H, NH), 8.08 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.61 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar), 7.34−7.60 (m, 7H, Ar), 7.12 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar), 6.97 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 2.34 (s, 3H, Me), 1.42 (s, 9H, *t*-Bu).^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 193.8, 186.2, 177.0, 172.3, 141.0, 140.5, 135.9, 130.8, 130.6, 130.3, 130.2, 129.5, 129.2, 128.8, 128.6, 128.4, 128.1, 126.6, 122.1, 39.5, 27.3, 21.0.HRMS (ESI$^-$), m/z: 639.0551 [M − H]$^-$. $C_{29}H_{27}Cl_2N_4O_2Pd$, Calcd m/z: 639.0546. IR spectrum (KBr, selected bands, cm^{-1}): 3469 w, ν(N−H), 3200, 3180, 3054 s, ν(C$_{Ar}$−H), 2972, 2928 s, ν(C−H), 1750 s, ν(C=O), 1675 m, ν(C=N), 1543 s, ν(N−C=N). Anal. Calcd for $C_{29}H_{28}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 54.52; H 4.58; N 10.25. Found: C 54.51; H 4.56; N 10.19.

11i. Yield 52%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.54 (s, 1H, NCN*H*), 10.86 (s, 1H, NH), 7.95 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.57 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar), 7.52 (m, 5H, Ar), 7.47 (d, $^3J_{HH}$ = 7.2 Hz, 4H, Ar), 7.35 (t, $^3J_{HH}$ = 7.2 Hz, 4H, Ar), 7.24−7.32 (m, 3H, Ar), 7.19 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar), 7.06 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ar), 6.98−7.02 (m, 1H, Ar), 5.63 (s, 1H, C*H*Ph$_2$), 2.11 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 192.7, 186.3, 172.3, 170.3, 140.6, 140.2, 140.2, 137.8, 136.3, 130.9, 130.6, 130.3, 130.2, 129.3, 129.1, 128.9, 128.8, 128.7, 128.4, 128.2, 128.0, 127.5, 125.0, 121.8, 56.6, 21.0. HRMS (ESI$^-$), m/z: 749.0716 [M − H]$^-$. $C_{38}H_{29}Cl_2N_4O_2Pd$, Calcd m/z: 749.0702. IR spectrum (KBr, selected bands, cm^{-1}): 3428, 3372 w, ν(N−H), 3168, 3056 s, ν(C−H$_{Ar}$), 2998 s, ν(C−H), 1766 s, ν(C=O), 1678 m, ν(C=N), 1532 s, ν(N−C=N). Anal. Calcd for $C_{38}H_{30}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 60.58; H 4.19; N 8.83. Found: C 60.56; H 4.17; N 8.76.

11j. Yield 58%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.03 (s, 1H, NCN*H*), 10.74 (s, 1H, NH), 8.08 (s, 1H, Ar), 7.85 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.59 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.20−7.50 (m, 12H, Ar, NH), 7.08 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 2.41 (s, 3H, Me), 2.32 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 195.0, 186.4, 172.6, 146.1, 141.0, 140.4, 138.1, 137.7, 131.0, 130.6, 130.4, 130.3, 130.2, 129.9, 129.5, 129.3, 129.0, 128.9, 128.3, 128.2, 127.3, 123.2, 21.8, 21.1. HRMS (ESI$^-$), m/z: 709.0064 [M − H]$^-$. $C_{31}H_{25}Cl_2N_4O_3SPd$, Calcd m/z: 709.0059. IR spectrum (KBr, selected bands, cm^{-1}): 3380, 3344 w, ν(N−H), 3198, 3046 s, ν(Ar−H), 2960, 2934 s, ν(C−H), 1684 m, ν(C=N), 1538 s, ν(N−C=N), 1374 s, ν(SO$_2$). Anal. Calcd for $C_{31}H_{26}Cl_2N_4O_3SPd{\cdot}CH_3CN$: C 52.64; H 3.88; N 9.30. Found: C 52.59; H 3.87; N 9.23.

12e. Yield 53%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.32 (s, 1H, NCN*H*), 10.95 (s, 1H, NH), 7.94 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.47 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.30−7.40 (m, 3H, Ar), 7.15−7.25 (m, 4H, Ar), 7.06 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 6.89 (s, 1H, NH), 2.46 (s, 3H, Me), 2.34 (s, 3H, Me), 1.47 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 194.6, 186.5, 176.6, 172.6, 143.4, 141.4, 141.4, 139.5, 139.3, 135.9, 130.9, 130.1, 129.2, 129.0, 128.9, 126.4, 125.8, 125.7, 125.2, 122.7, 39.6, 27.3, 21.6, 21.6.HRMS (ESI$^-$), m/z: 653.0719 [M − H]$^-$. $C_{30}H_{29}Cl_2N_4O_2Pd$, Calcd m/z: 653.0702. IR spectrum (KBr, selected bands, cm^{-1}): 3400 w, ν(N−H), 2976 s, ν(C−H), 1760, 1781 s, ν(C=O), 1681 m, ν(C=N) 1525 s, ν(N−C=N). Anal. Calcd for $C_{30}H_{30}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 55.15; H 4.77; N 10.05. Found: C 55.13; H 4.71; N 9.98.

12f. Yield 48%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.27 (s, 1H, NCN*H*), 10.89 (s, 1H, NH), 7.56 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.42−7.52 (m, 9H, Ph), 7.31−7.39 (m, 6H, Ar), 7.30 (s, 1H, Ar), 7.27 (s, 1H, Ar), 7.16−7.24 (m, 2H, Ar), 6.86−6.92 (m, 1H, Ar), 6.78 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 5.60 (s, 1H, C*H*Ph$_2$), 2.45 (s, 3H, Me), 2.17 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 193.1, 186.9, 172.5, 169.9, 142.6, 141.2, 141.0, 140.1, 139.0, 137.7, 130.8, 130.2, 129.4, 129.0, 128.9, 128.8, 128.3, 127.5, 125.9, 125.7, 125.4, 124.8, 122.0, 56.6, 21.6, 21.4. HRMS (ESI$^+$), m/z: 763.0879 [M − H]$^-$. $C_{39}H_{31}Cl_2N_4O_2Pd$, Calcd m/z: 763.0859. IR spectrum (KBr, selected bands, cm^{-1}): 3468, 3423 w, ν(N−H), 3160, 3108, 3062, 3032 s, ν(C$_{Ar}$−H), 2952, 2923 s, ν(C−H), 1760, 1774 s, ν(C=O), 1675 m, ν(C=N) 1542 s, ν(N−C=N). Anal. Calcd for $C_{39}H_{32}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 61.02; H 4.37; N 8.68. Found: C 61.04; H 4.39; N 8.61.

12g. Yield 46%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.70 (s, 1H, NCN*H*), 10.99 (s, 1H, NH), 8.44 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 8.26 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar), 7.85 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.47 (m, 4H, Ar), 7.36 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.26 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.13 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 2.46 (s, 3H, Me), 2.39 (s, 3H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ, ppm): 194.3, 186.5, 172.7, 164.2, 142.3, 141.7, 139.4, 138.9, 132.5, 131.8, 131.4, 131.4, 131.1, 130.0, 129.6, 129.4, 129.0, 128.7, 126.5, 125.7, 125.6, 125.0, 117.6, 112.6, 109.7, 21.60, 21.57. HRMS (ESI$^-$), m/z: 698.0358 [M − H]$^-$. $C_{33}H_{24}Cl_2N_5O_2Pd$, Calcd m/z: 698.0342. IR spectrum (KBr, selected bands, cm^{-1}): 3182 m, ν(C$_{Ar}$−H), 2998 m, ν(C−H), 2246 w, ν(C≡N), 1747 s, ν(C=O), 1686 s, ν(C=N), 1609 m, ν(C=N), 1527 s, ν(N−C=N). Anal. Calcd for $C_{33}H_{25}Cl_2N_5O_2Pd{\cdot}CH_3CN$: C 56.66; H 3.80; N 11.33. Found: C 56.64; H 3.76; N 11.26.

12h. Yield 58%, brown crystals. ^{1}H NMR ($CDCl_3$, δ, ppm): 11.29 (s, 1H, NCN*H*), 10.87 (s, 1H, NH), 7.97 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.35 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.30 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.14 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.09 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.01 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar), 6.97 (s, 1H), 2.45(s, 3H, Me), 2.36 (s, 3H, Me), 2.36 (s, 3H,

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Me), 1.44 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 194.0, 186.2, 176.9, 172.5, 141.4, 141.0, 139.7, 139.3, 135.8, 131.0, 130.1, 129.6, 129.2, 128.8, 128.7, 126.5, 126.0, 125.3, 122.3, 39.6, 27.3, 21.6, 21.6, 21.0. HRMS (ESI^-), *m*/*z*: 667.0871 $[M - H]^-$. $C_{31}H_{31}Cl_2N_4O_2Pd$, Calcd *m*/*z*: 667.0859. IR spectrum (KBr, selected bands, cm^{-1}): 3390 w, ν(N−H), 3174, 3038 s, $\nu(C_{Ar}-H)$, 2973 s, ν(C−H), 1755 s, ν(C=O), 1678 m, ν(C=N), 1536 s, ν(N−C=N). Anal. Calcd for $C_{31}H_{32}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 55.75; H 4.96; N 9.85. Found: C 55.73; H 4.94; N 9.78.

12i. Yield 58%, brown crystals. ^1H NMR ($CDCl_3$, δ, ppm): 11.57 (s, 1H, NCN*H*), 10.92 (s, 1H, NH), 7.93 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.49 (m, 6H, Ar), 7.32−7.40 (m, 8H, Ar), 7.29 (s, 1H, Ar), 7.25−7.28 (m, 1H, Ar), 7.13 (s, 1H, Ar), 7.50−7.10 (m, 2H, Ar), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 5.67 (s, 1H, C*H*Ph_2), 2.45 (s, 3H, Me), 2.29 (s, 3H, Me), 2.21 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 192.9, 186.2, 172.6, 170.3, 141.5, 141.5, 140.5, 139.5, 139.2, 137.8, 136.1, 131.0, 130.1, 129.3, 129.2, 128.9, 128.8, 128.8, 128.3, 127.4, 125.9, 125.2, 125.1, 122.0, 34.9, 21.6, 21.1, 18.9. HRMS (ESI^-), *m*/*z*: 776.0943 $[M - H]^-$. $C_{40}H_{32}Cl_2N_4O_2Pd$, Calcd *m*/*z*: 776.0937. IR spectrum (KBr, selected bands, cm^{-1}): 3474, 3422 w, ν(N−H), 3164, 3030 s, $\nu(C_{Ar}-H)$, 2964, 2918 s, ν(C−H), 1772 s, ν(C=O), 1673 m, ν(C=N) 1547 s, ν(N−C=N). Anal. Calcd for $C_{40}H_{33}Cl_2N_4O_2Pd{\cdot}CH_3CN$: C 61.59; H 4.31; N 8.55. Found: C 61.58; H 4.28; N 8.49.

12j. Yield 59%, red crystals. ^1H NMR ($CDCl_3$, δ, ppm): 11.03 (s, 1H, NCN*H*), 10.83 (s, 1H, NH), 7.85−7.90 (m, 3H, Ar), 7.48 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.37 (m, 4H, Ar), 7.32 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar), 7.12−7.17 (m, 2H, Ar), 7.08 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 2.42 (s, 3H, Me), 2.39 (s, 3H, Me), 2.35 (s, 6H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 194.9, 186.4, 172.7, 169.8, 146.0, 141.2, 139.6, 138.5, 137.5, 131.2, 130.8, 130.3, 130.1, 129.6, 129.3, 129.1, 129.0, 128.9, 127.1, 126.1, 125.3, 123.5, 21.8, 21.6, 21.5, 21.1. HRMS (ESI^-), *m*/*z*: 737.0378 $[M - H]^-$. $C_{33}H_{29}Cl_2N_4O_3SPd$, Calcd *m*/*z*: 737.0372. IR spectrum (KBr, selected bands, cm^{-1}): 3388 w, ν(N−H), 3190, 3040 s, $\nu(C_{Ar}-H)$, 2976, 2918 s, ν(C−H), 1674 m, ν(C=N), 1538 s, ν(N−C=N), 1390 s, $\nu(SO_2)$. Anal. Calcd for $C_{33}H_{30}Cl_2N_4O_3SPd{\cdot}CH_3CN$: C 53.82; H 4.26; N 8.97. Found: C 53.79; H 4.23; N 8.90.

13e. Yield 46%, brown crystals. ^1H NMR ($CDCl_3$, δ, ppm): 11.11 (s, 1H, NCN*H*), 10.71 (s, 1H, NH), 7.84 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar), 7.56 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.43 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.34 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.16 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.11 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar), 7.04 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 6.72 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 3.88 (s, 3H, OMe), 3.78 (s, 3H, OMe), 1.44 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 194.3, 187.0, 176.6, 172.8, 161.5, 161.4, 143.3, 138.4, 137.8, 132.0, 130.9, 129.0, 129.0, 126.3, 125.7, 122.6, 121.4, 120.4, 115.7, 114.0, 55.6, 55.4, 39.5, 27.3. HRMS (ESI^+), *m*/*z*: 685.0617 $[M - H]^-$. $C_{30}H_{29}Cl_2N_4O_4Pd$, Calcd *m*/*z*: 685.0601. IR spectrum (KBr, selected bands, cm^{-1}): 3356 w, ν(N−H), 3176, 3040 s, $\nu(C_{Ar}-H)$, 2972 s, ν(C−H), 1757 s, ν(C=O), 1678 m, ν(C=N) 1521 s, ν(N−C=N). Anal. Calcd for $C_{30}H_{30}Cl_2N_4O_4Pd{\cdot}CH_3CN$: C 52.72; H 4.56; N 9.61. Found: C 52.70; H 4.53; N 9.54.

13f. Yield 47%, brown crystals. ^1H NMR ($CDCl_3$, δ, ppm): 11.36 (s, 1H, NCN*H*), 10.81 (s, 1H, NH), 7.78 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar),7.45−7.55 (m, 11H, Ar), 7.34−7.38 (m, 9H, Ar), 7.18−7.24 (m, 4H, Ar), 6.51 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 5.65 (s, 1H, C*H*Ph_2), 3.88 (s, 3H, OMe), 3.67 (s, 3H, OMe).$^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 192.9, 187.2, 172.8, 169.9, 161.4, 161.3, 142.5, 138.1, 138.0, 137.7, 131.9, 131.2, 129.0, 129.0, 128.9, 128.8, 128.4, 127.5, 125.8, 124.6, 122.1, 121.3, 120.5, 115.6, 55.6, 55.2, 30.9. HRMS (ESI^-), *m*/*z*: 795.0774 $[M - H]^-$. $C_{39}H_{31}Cl_2N_4O_4Pd$, Calcd *m*/*z*: 795.0757. IR spectrum (KBr, selected bands, cm^{-1}): 3410 w, ν(N−H), 3180, 3056, 3029, 3002 s, $\nu(C_{Ar}-H)$, 2838 s, ν(C−H), 1765 s, ν(C=O), 1676 m, ν(C=N) 1520 s, ν(N−C=N). Anal. Calcd for $C_{39}H_{32}Cl_2N_4O_4Pd{\cdot}CH_3CN$: C 58.69; H 4.20; N 8.35. Found: C 58.66; H 4.19; N 8.28.

13h. Yield 54%, brown crystals. ^1H NMR ($CDCl_3$, δ, ppm): 11.23 (s, 1H, NCN*H*), 10.78 (s, 1H, NH), 7.97 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.61 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.39 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.14 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.06 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 6.99 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar), 6.79 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 3.90 (s, 3H, OMe), 3.82 (s, 3H, OMe), 2.35 (s, 3H, Me), 1.44 (s, 9H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 193.9, 186.8, 176.9, 172.8, 161.5, 161.4, 140.9, 138.6, 137.7, 135.8, 132.0, 130.8, 129.5, 128.7, 126.5, 122.2, 121.5, 120.4, 115.8, 114.0, 55.6, 55.4, 39.5, 27.3, 21.1. HRMS (ESI^-), *m*/*z*: 699.0782 $[M - H]^-$. $C_{31}H_{31}Cl_2N_4O_4Pd$, Calcd *m*/*z*: 699.0757. IR spectrum (KBr, selected bands, cm^{-1}): 3358 w, ν(N−H), 3172, 3032 s, $\nu(C_{Ar}-H)$, 2970, 2930, 2838 s, ν(C−H), 1754 s, ν(C=O), 1677 m, ν(C=N) 1521 s, ν(N−C=N). Anal. Calcd for $C_{31}H_{32}Cl_2N_4O_4Pd{\cdot}CH_3CN$: C 53.35; H 4.75; N 9.43. Found: C 53.33; H 4.74; N 9.36.

13i. Yield 55%, brown crystals. ^1H NMR ($CDCl_3$, δ, ppm): 11.58 (s, 1H, NCN*H*), 10.91 (s, 1H, NH), 7.97 (d, $^4J_{HH}$ = 1.6 Hz, 1H, Ar), 7.57 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.50 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar), 7.42 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.37 (t, $^3J_{HH}$ = 7.6 Hz, 4H, Ar), 7.25−7.30 (m, 1H, Ar), 7.15 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar), 7.08 (t, $^3J_{HH}$ = 8.0 Hz, 4H, Ar), 6.72 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 5.68 (s, 1H, C*H*Ph_2), 3.90 (s, 3H, OMe), 3.76 (s, 3H, OMe) 2.25 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 192.9, 186.9, 172.9, 170.3, 161.6, 161.5, 143.5, 140.5, 138.6, 137.8, 137.3, 136.0, 131.9, 130.7, 129.2, 128.9, 128.8, 128.8, 128.3, 127.5, 125.0, 121.9, 120.3, 115.8, 114.0, 62.7, 55.6, 55.4, 21.0. HRMS (ESI^-), *m*/*z*: 809.0919 $[M - H]^-$. $C_{40}H_{33}Cl_2N_4O_4Pd$, Calcd *m*/*z*: 809.0913. IR spectrum (KBr, selected bands, cm^{-1}): 3412 w, ν(N−H), 3178, 3058, 3029 s, $\nu(C_{Ar}-H)$, 2930, 2836 s, ν(C−H), 1762 s, ν(C=O), 1659 m, ν(C=N), 1520 s, ν(N−C=N). Anal. Calcd for $C_{40}H_{34}Cl_2N_4O_4Pd{\cdot}CH_3CN$: C 59.13; H 4.37; N 8.21. Found: C 59.10; H 4.33; N 8.15.

13j. Yield 52%, brown crystals. ^1H NMR ($CDCl_3$, δ, ppm): 10.96 (s, 1H, NCN*H*), 10.66 (s, 1H, NH), 7.85−7.90 (m, 2H, Ar), 7.57 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 7.49 (s, 1H, NH), 7.43 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.34 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar), 7.32 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar), 7.11 (s, $^3J_{HH}$ = 8.4 Hz, 1H, Ar), 7.03 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 6.77 (d, $^3J_{HH}$ = 8.8 Hz, 2H, Ar), 3.84 (s, 3H, OMe), 3.81 (s, 3H, OMe), 2.40 (s, 3H, Me), 2.32 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 194.8, 140.7, 138.7, 138.5, 137.7, 137.4, 134.7, 131.9, 131.6, 131.3, 130.8, 130.5, 130.3, 129.6, 129.3, 128.9, 128.4, 126.8, 123.6, 121.5, 120.4, 115.8, 114.0, 55.5, 55.4, 21.8, 21.1. HRMS (ESI^-), *m*/*z*: 769.0286 $[M - H]^-$. $C_{33}H_{29}Cl_2N_4O_5SPd$, Calcd *m*/*z*: 769.0270. IR spectrum (KBr, selected bands, cm^{-1}): 3392 w, ν(N−H), 3178, 3042 s, $\nu(C_{Ar}-H)$, 2994, 2964 s, ν(C−H), 1676 m, ν(C=N), 1520 s, ν(N−C=N), 1376 s, $\nu(SO_2)$. Anal. Calcd for $C_{33}H_{30}Cl_2N_4O_5SPd{\cdot}CH_3CN$: C 51.70; H 4.09; N 8.61. Found: C 51.68; H 4.08; N 8.53.

X-ray Structure Determinations. The crystals of **4c**·CH_2Cl_2, **9a**, **10c**·H_2O·0.5CH_2Cl_2, and **11j**·CH_3CN were obtained by a slow evaporation of solvent at room temperature. Crystals of compounds **4c**·CH_2Cl_2, **9a**, **10c**·H_2O·0.5CH_2Cl_2, and **11j**·CH_3CN were immersed in cryo-oil, mounted in a nylon loop, and analyzed at a temperature of 100 K. The X-ray diffraction data were collected on an Agilent Technologies Excalibur Eos and Supernova Atlas diffractometers. The temperature for all experiments was kept at 100 K. The structures have been solved by the direct methods and refined by means of the SHELXL−97[21] program incorporated in the OLEX2 program package.[22] The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the "riding" model approximation, with U_{iso}(H) set to1.5U_{eq}(C) and C−H 0.96 Å for CH_3 groups, U_{iso}(H) set to 1.2U_{eq}(C) and C−H 0.93 Å for the CH groups, and U_{iso}(H) set to 1.2U_{eq}(N) and N−H 0.86 Å for the NH groups. Empirical absorption correction was applied in CrysAlisPro program complex[23] using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The crystal structures and crystallographic details are given in Table S2. Crystal data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers CCDC 1818370, CCDC 1817631, CCDC 1817212, and CCDC 1822187 for **4c**·CH_2Cl_2, **9a**, **10c**·H_2O·0.5CH_2Cl_2, and **11j**·CH_3CN, respectively.

Computational Details. The full geometry optimization, total energies, MO energies and composition, and electron transitions in the UV−vis spectra have been carried out at the DFT hybrid level of theory using Becke's three parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP)[24−27] and standard basis 6-31+G(d,p) for

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light atoms and pseudopotential CEP 1−21G[28] for palladium using the Gaussian 03[29] program package. Natural charges have been determined by NBO analysis.[30] Twenty singlet vertical electron transitions in UV spectra have been calculated by time-dependent method.[31]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00725.

Experimental data for characterization of **4**−**6** and **11**−**13**, NMR, UV−vis absorption, and emission spectra, crystallographic table for **4c**·CH_2Cl_2, **9a**, **10c**·H_2O·0.5CH_2Cl_2, and **11j**·CH_3CN, and computational details for **4c**, **11j**, and **12e** (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 1817212, 1817631, 1818370, and 1822187 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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