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Novel Reactivity Mode of Metal Diaminocarbenes: Palladium(II)-Mediated Coupling between Acyclic Diaminocarbenes and Isonitriles Leading to Dinuclear Species

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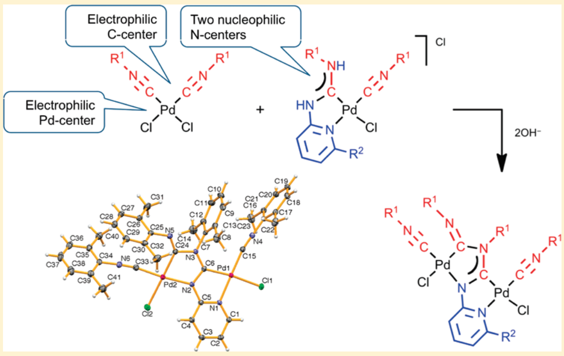
Supporting Information



ABSTRACT: Metal-mediated coupling between equimolar amounts of *cis*-[$PdCl_2(CNR^1)_2$] [R^1 = 2,6-$Me_2C_6H_3$ (Xyl) **1**, 2-Cl,6-Me-C_6H_3 **2**, cyclohexyl (Cy) **3**] and $H_2NC_5H_3R^2N$ [R^2 = H, 2-aminopyridine **4**; R^2 = NH_2, 2,6-diaminopyridine **5**] proceeds smoothly for 12 h at 20−25 °C and leads to the diaminocarbene species [$PdCl\{\underline{C}(NHC_5H_3R^2\underline{N})=N(H)R^1\}(CNR^1)$]Cl (**6**−**9**). In the reaction of **2** with **5** (1:1 molar ratio), corresponding carbene **10** was detected only by high-resolution ESI$^+$-MS in a mixture with other yet unidentified products. Addition of each of **6**−**8** to starting **1** or **2** (1:1 molar ratio) in the presence of excess solid K_2CO_3 in $CHCl_3$ and heating of the reaction mixture for 12 h at 40 °C led to a novel type of dinuclear complexes, **11** (75% isolated yield) and **13** (65%). Similar dinuclear complexes **12** and **14**, formed by addition of **7** or **10** to **2**, were identified by high-resolution ESI$^+$-MS in the mixture with other species (e.g., **7** and **10**). Generation of **11**−**14** proceeds via a cascade reaction including addition of the amino group of a 2-aminopyridine to the metal-activated isonitrile, ring-closure, and coupling of the derived acyclic diaminocarbene complex with the yet unreacted starting material. Complexes **6**−**9**, **11**, and **13** were fully characterized by elemental analyses (C, H, N), high-resolution ESI$^+$-MS, IR, and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopies, while **10**, **12**, and **14** were identified by ESI$^+$-MS. In addition, the structures of five complexes [**6**, **6a** (the latter is a neutral species derived from the deprotonation of **6**), **9**, **11**, and **13**] were elucidated by single-crystal X-ray diffraction.

INTRODUCTION

In the past decade, metal-aminocarbenes gained special attention in both organometallic and organic chemistry.[1−6] In particular, complexes with N-heterocyclic carbenes [M](NHC)[1,7−10] and, to a lesser extent so far, structurally relevant acyclic diaminocarbene [M](ADC) species[6,11−23] (Figure 1) have revolutionized catalysis of a number of useful organic transformations.[8,24] It is therefore not surprising that the number of studies on NHCs and ADCs dramatically increased in recent years. Most of work in this field is devoted to the preparation of novel metal-aminocarbenes, optimization of the electronic and steric effects of the carbenes in their complexes, understanding the nature of the metal−$C_{carbene}$ bond, and, what is also very important, the application of carbene metal species as catalysts in organic syntheses. A significant number of publications on metal-aminocarbenes are summarized in excellent reviews related to the preparation[2,3,5,6,11] and catalytic applications[10,24] of these compounds.

Although metal-aminocarbenes have been prepared for a long time [starting from pioneering works of Chugaev,[25] when they could not be recognized as such, and later by Richards[26]], the reactivity modes of aminocarbene ligands are practically unknown. A few reports in this direction[27−30] [see also a review[31]] indicate that the NH moieties of diaminocarbenes (and of related aminooxycarbenes) exhibit a significant Brønsted acidity and can be deprotonated either by action of bases or electrochemically.

Recently, within our project on the nucleophilic addition to metal-activated substrates bearing CN triple bonds [i.e., nitriles

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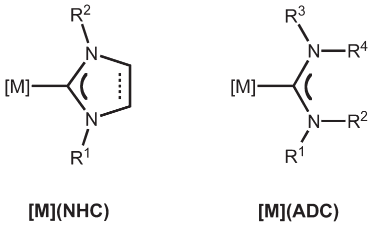


Figure 1. Complexes with N-heterocyclic carbene ([M](NHC)) and acyclic diaminocarbene ([M](ADC)) ligands.

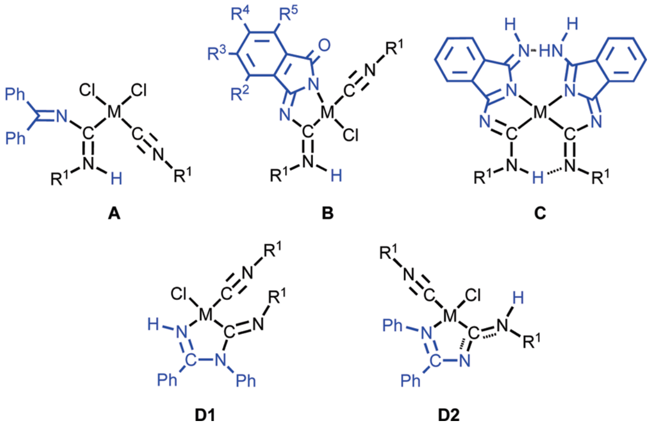


Figure 2

and isonitriles; for our reviews see refs 11 and 32−37], we reported the coupling of metal-bound isonitriles with sp^2-N nucleophiles, such as benzophenone imine (Figure 2, **A**),[38] 3-iminoisoindolin-1-one (**B**),[39−41] diiminoisoindoline (**C**),[42] and *N*-Ph-benzamidine (**D1** and **D2**; two regiosiomers are given),[43] furnishing a novel type of [M](ADCs). Some of these species are highly efficient in Suzuki−Miyaura[42] and Sonogashira reactions.[43]

We found that when the nucleophiles bear the amidine N═C−N moiety, the reaction leads to *aminocarbene-like* species with distinct single and double bonds in the CN$_2$ moiety, thus contrasting with typical diaminocarbenes, which exhibit bond delocalization (Figure 1). As a continuation of these works, it seemed logical to study other systems with various N═C−N groups, and we turned our attention to amino- and diaminopyridines as nucleophiles. These systems were previously investigated by Balch et al.[27] and also by Belluco et al.,[44,45] who described the coupling reactions with RNC at Pt centers, leading to the monodentate (**E**, Figure 3) and chelated (**F1**, **F2**) diaminocarbenes.[44,45]

Insofar as X-ray studies of complexes shown in Figure 3 were not performed, we decided to fill this gap and also to extend the number of such complexes. To our surprise, in addition to the findings reported in refs 27, 44, and 45 and fully confirmed in our study, we discovered that the chelated *diaminocarbenes* shown in Scheme 1 (see later) under certain conditions could themselves *behave as nucleophiles* and be involved in a cascade reaction with metal-activated isonitriles, thus forming dinuclear complexes. In this article, we disclose our observations and report on this novel reactivity mode of diaminocarbene ligands.

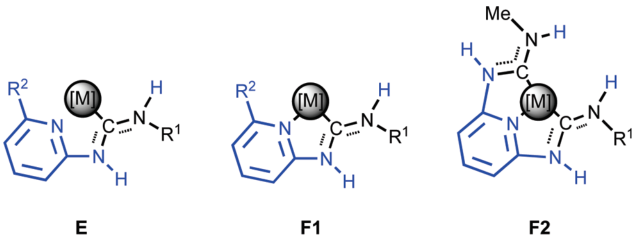


Figure 3. Different product patterns obtained from the coupling of metal-bound isonitriles with aminopyridines.

■ RESULTS AND DISCUSSION

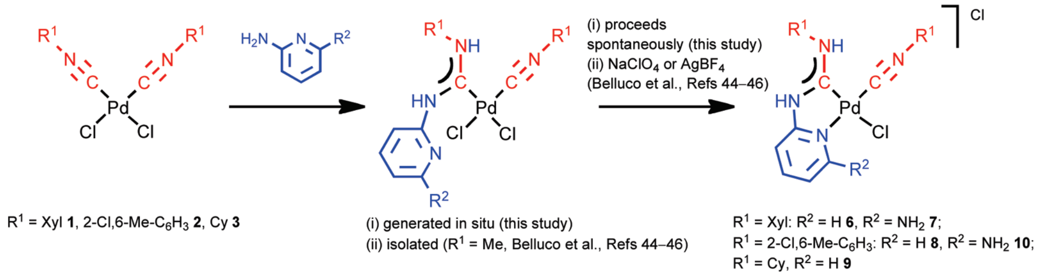
Generation of Diaminocarbenes via Addition of 2-Aminopyridines to (RNC)$_2$Pd^{II} Species. Previously Belluco and colleagues[44−46] reported on the reaction of an isonitrile in either the mononuclear *cis*-[PdCl$_2$(CNMe)$_2$][44,45] or halogen-bridged dinuclear [PdCl$_2$(CNPh)]$_2$[46] complexes and 2-aminopyridine (1:1 molar ratio, at room temperature, overnight), yielding mononuclear acyclic diaminocarbene complexes (70−80%). These species are derived from the addition of the amine functionality to the CN bond of a coordinated isonitrile. It was reported[46] that the pyridine N atom remains uncoordinated (step 1, Scheme 1), and its ligation could be achieved only by a further treatment with NaClO$_4$ or AgBF$_4$ (step 2).

As an extension of these studies to various isonitrile complexes and aminopyridines, we investigated the interplay between *cis*-[PdCl$_2$(CNR^1)$_2$] [R^1 = 2,6-Me$_2$C$_6$H$_3$ (Xyl) **1**, 2-Cl-6-Me-C$_6$H$_3$ **2**, cyclohexyl (Cy) **3**] and two 2-aminopyridines, i.e., 2-aminopyridine (**4**) and 2,6-diaminopyridine (**5**); combinations of these reactants were not previously studied. Dropwise addition of a CHCl$_3$ solution of **4** or **5** to each of **1**−**3** (1:1 molar ratio) leads to the immediate color change from pale yellow to intense lemon-yellow (for **4**) or orange (for **5**), followed by the dissolution of solid **1**−**3**. After 12 h at 20−25 °C, the reaction mixture contained **6**−**9** (Scheme 1), which were isolated in good (60−75%) yields. When **2** was treated with **5** (1:1 molar ratio), we detected complex **10** only by high-resolution ESI$^+$-MS along with a broad mixture of other yet unidentified products. Thus, the interplay between **2** and **5** in CHCl$_3$ in the temperature range 20−45 °C led to formation of a dark orange, oily residue comprising a broad mixture of products (five spots on TLC). The presence of **10** among other products (four spots on TLC) was detected by high-resolution ESI$^+$-MS, but, unfortunately, we were unable to isolate **10** as an individual species and, consequently, characterize it by NMR and elemental analyses. Furthermore, **3** does not react with **5** upon reflux in CHCl$_3$. The change of the solvent to MeNO$_2$ and increase of the temperature to 80 °C brings about decomposition of the starting materials.

We found that our systems, in contrast to those studied by the Italian group,[44,45] are more reactive, and generation of **6**−**10** is accompanied by other intriguing processes disclosed in sections given below, while in the next section we describe the identification of **6**−**10**.

Characterization of ***6***−***10***. Complexes **6**−**9** were fully characterized by elemental analyses (C, H, N), IR, high-resolution ESI$^+$-MS, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. Complex **10** was identified in their mixture with other species (e.g., **14**, see later) by high-resolution ESI$^+$-MS. The ESI$^+$ mass spectra of **6**−**10** display the molecular ion peaks [M]$^+$ or a fragmentation corresponding to the loss of Cl from the molecular ion, viz., [M − Cl]$^+$, with the characteristic isotopic distribution.

Scheme 1. Conventional Addition of Pyridine-2-amine-6-R^2 to an Isonitrile Ligand in *cis*-[$PdCl_2(CNR^1)_2$] and Subsequent Ring Closure



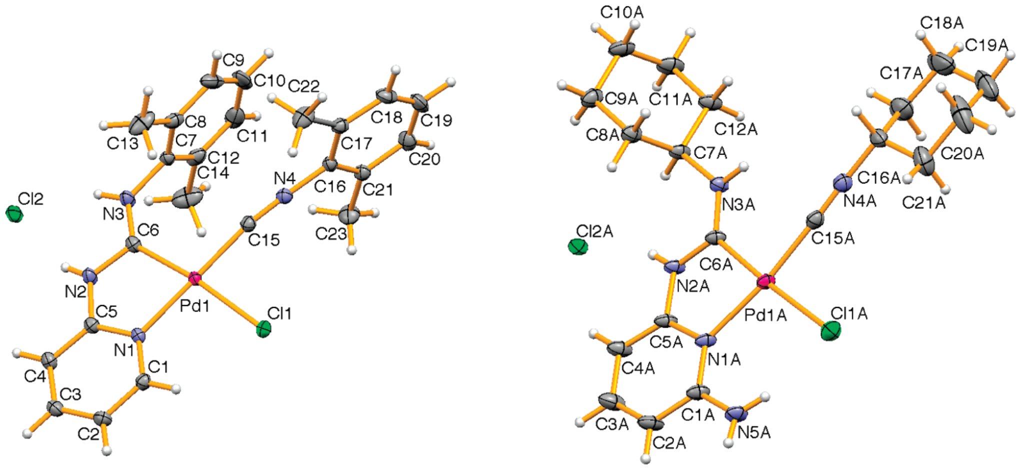


Figure 4. View of **6** and **9** (form A) with the atomic numbering schemes. Thermal ellipsoids are drawn with 50% probability. Hydrogen labels are omitted for simplicity.

The ^{1}H NMR spectra of **6**−**9** exhibit two broad singlets in the δ 13.5−12.1 range from the NH protons and a set of overlapped resonances (δ 9.0−6.1) assigned to the aromatic C−H protons. Two singlets corresponding to the Me groups of **6**−**8** emerge in the ^{1}H NMR in the range δ 2.5−2.2 and in the $^{13}C\{^1H\}$ NMR in the δ 19.3−18.5 range. In the ^{1}H NMR spectrum of **9**, the characteristic signals of the protons of the tertiary group from the cyclohexyl rings emerge at 4.3 and 4.2 ppm. In the $^{13}C\{^1H\}$ NMR spectra of **6**−**9**, the $C_{carbene}{=}NH$ signals were found to resonate in the range from 188 to 172 ppm. These values are more downfield than the values that fall in the interval of 157−159 ppm, reported for the series of chelated N-heterocyclic carbenes, such as bis(imidazolylidene) palladium dichloride complexes, but are upfield of the 194−227 ppm range found for the palladium-bound monodentate acyclic diaminocarbenes and are close to the typical values for coordinated NHCs obtained by the [2 + 3] cycloaddition of nitrones to coordinated isonitriles (ca. 170 ppm).[47]

Each of the IR spectra of **6**−**9** displays one strong $\nu(C{\equiv}N)$ stretching vibration at 2239−2217 cm^{-1}. In the carbene moieties, a strong band due to $\nu(C{=}N)$ appears between 1653 and 1568 cm^{-1}. The medium-intensity band at 3447−3323 cm^{-1} is characteristic of $\nu(N{-}H)$ vibrations, while a strong-intensity band due to δ(C−H from Ar) is displayed at 785−772 cm^{-1}.

The cationic complexes **6** and **9** and corresponding deprotonated neutral complex **6a** (one crystal of **6a** was obtained from the mixture with **6**) were characterized by X-ray single-crystal diffraction (Figure 4 and Table 1; Figure 1S and Tables 1S and 2S, Supporting Information), and the obtained data reveal both the addition of **4** to one isonitrile ligand (while the other RNC ligand remains intact) and coordination of the pyridine ring to the Pd^{II} center. In the crystal structure of **9**, two slightly different independent molecules (A and B) were detected; a mean value of both was used for a further comparison (see Supporting Information for detailed examination of the X-ray data).

In both diaminocarbene complexes **6** and **9**, the slightly distorted square-planar geometry around the metal center is completed with one bidentate diaminocarbene ligand, one isonitrile (in the *cis*-position to the carbene moiety), and one chloride. In the palladacycle, the $Pd{-}C_{carbene}$ distances [Pd1−C6: 1.986(2) Å for **6**, 1.972(2) Å for **9**] are slightly longer (for **6**) or equal within 3σ to those in the related *cis*-[$PdCl_2\{C(OMe){=}N(H)Me\}_2$] (1.953−1.972 Å)[48] and *cis*-[$PdCl_2\{\underline{C}({=}NHCy)NHNH\underline{C}({=}NHCy)\}_2$] (1.958−1.964 Å)[49] complexes. The newly formed carbene ligands adopt the *Z* (for **6**) or *E* (for **9**) configuration, correspondingly, and the $NC_{carbene}N$ moiety is roughly planar. In the latter moiety, the C6−N2 and C6−N3 bond lengths [1.358(2) and 1.309(2) Å for **6**, 1.337(3) and 1.314(3) Å for **9**] are nearly equal and are intermediate between typical single and typical double bonds,[50] indicating a bond delocalization that is typical for the diaminocarbene systems.

In **6a**, the slightly distorted square-planar geometry around the metal center is completed with one bidentate aminocarbene-derived ligand [Pd1−C6: 1.993(2) Å], one isonitrile, and one chloride. The aminocarbene-derived ligand (obtained via the deprotonation of the original diaminocarbene species) is in the *Z*-configuration. The NCN_{Xyl} moiety is roughly planar, and the NC bonds [C6−N2 1.391(3) Å and C6−N3 1.279(3) Å] are close to a normal single and a normal double bond, correspondingly, indicating the difference as compared to typical diaminocarbene species **6** and **9**.

Coupling between ADCs and Isonitriles. Addition of each of ADCs **6**−**8** to starting **1** or **2** (1:1 molar ratio) in the presence of excess solid K_2CO_3 in $CHCl_3$ and heating of the reaction mixture at 40 °C for 12 h led to novel products **11** and **13** (Scheme 2, Table 2), which were isolated in good (**11**, 75%; **13**, 65%) yields. The similar dinuclear complexes **12** and **14**, formed by the addition of **8** or **10** to **2**, were identified by high-resolution ESI^+-MS in the mixture with other species (e.g., **8** or **10**, correspondingly). We were not, however, able to isolate **12** and **14** as individual substances (in the case of **14**, presumably due to an insufficient purity of starting **10**) and, consequently, characterize them with the use of NMR and elemental analyses.

We believe that the generation of **11**−**14** proceeds by addition of Belluco-type ADC complexes with two nucleophilic N centers to both electrophilic centers (a ligated isonitrile carbon and the metal) of the starting isonitrile complexes (Scheme 3). This overall cascade reaction includes the addition of the amino group of a 2-aminopyridine to the metal-activated isonitrile moiety, ring closure, and the coupling of the derived ADC complex with the yet unreacted starting material.

This process is facilitated upon addition of K_2CO_3, which serves as a base, assisting deprotonation of the HN carbene moiety and thus increasing the nucleophilic activity of the N_2C group. Complexes **11**−**14** are also formed in the syntheses of **6**−**10** without the base, but their formation is then not selective, leading to a mixture of species (five spots on TLC), where **11**−**14** were generated in ca. 10−15% NMR yields.

Characterization of Dinuclear Complexes ***11***−***14***. Complexes **11** and **13** were characterized by elemental (C, H, N) analyses, high-resolution ESI^+-MS, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies, while **12** and **14** were detected by high-resolution ESI^+-MS monitoring of the reaction mixtures. In addition, the

Table 1. Selected Bond Lengths [Å] and Angles [deg] for 6 and 9 (mean value of forms A and B)

	6	9 (A + B)
Pd(1)−Cl(1)	2.3255(4)	2.3755(6)
Pd(1)−N(1)	2.043(1)	2.084(2)
Pd(1)−C(6)	1.986(2)	1.972(2)
Pd(1)−C(15)	1.940(2)	1.945(2)
N(1)−C(1)	1.350(2)	1.360(3)
N(1)−C(5)	1.346(2)	1.362(3)
N(2)−C(5)	1.379(2)	1.391(3)
N(2)−C(6)	1.358(2)	1.337(3)
N(3)−C(6)	1.309(2)	1.314(3)
N(3)−C(7)	1.435(2)	1.477(3)
N(4)−C(15)	1.147(2)	1.141(3)
C(6)−Pd(1)−Cl(1)	172.33(4)	176.41(7)
C(15)−Pd(1)−N(1)	179.45(6)	170.1(1)
C(6)−Pd(1)−N(1)	80.53(6)	80.34(8)
N(1)−Pd(1)−Cl(1)	94.21(4)	102.96(5)
C(15)−Pd(1)−Cl(1)	86.11(5)	85.18(9)
C(15)−Pd(1)−C(6)	99.20(6)	91.5(1)
C(6)−N(2)−C(5)	119.7(1)	119.5(2)
N(2)−C(6)−Pd(1)	111.9(1)	113.3(2)
N(3)−C(6)−Pd(1)	133.0(1)	126.8(2)
N(3)−C(6)−N(2)	115.0(1)	120.0(2)
C(6)−N(3)−C(7)	126.4(1)	127.0(2)
C(15)−N(4)−C(16)	177.2(2)	173.4(3)
N(4)−C(15)−Pd(1)	170.5(1)	176.0(3)

Scheme 2. Reaction of 1 or 2 with 6−8

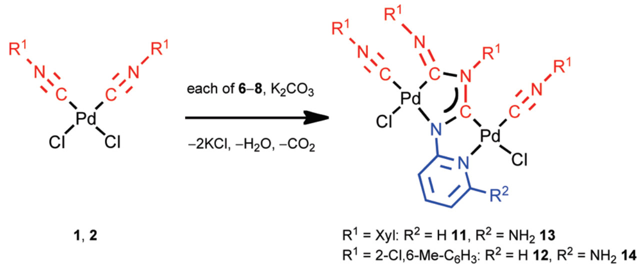
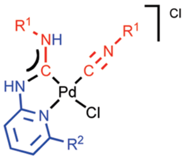
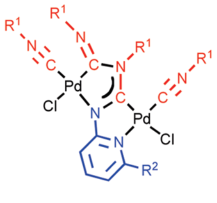
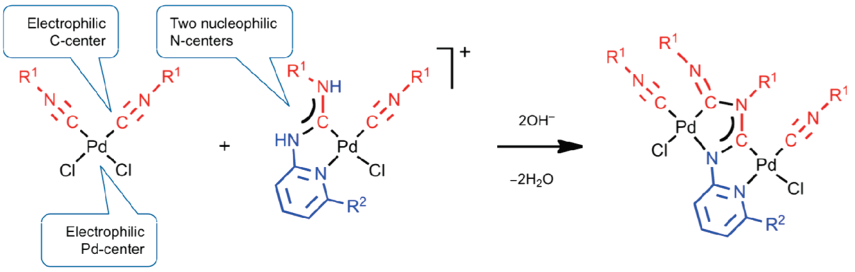


Table 2. Numbering of Complexes Given in Scheme 2

Pd complexes	R^1 in **6**, **7**, **11**, and **12** (R^2 = H)	R^1 in **8**–**10**, **13**, and **14** ($R^2 = NH_2$)
	Xyl (**6**)	Xyl (**8**)
	2-Cl,6-Me-C_6H_3 (**7**)	2-Cl-6-Me-C_6H_3 (**10**)
	–	Cy (**9**)
	Xyl (**11**)	Xyl (**13**)
	2-Cl,6-Me-C_6H_3 (**12**)	2-Cl-6-Me-C_6H_3 (**14**)

Scheme 3. **Nucleophilic Addition of the Complexed ADCs to Metal-Activated Isonitriles**



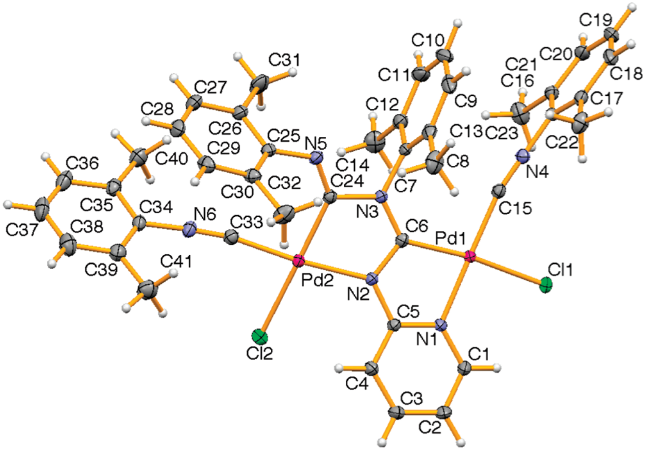


Figure 5. View of **11** with the atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Hydrogen labels are omitted for simplicity.

structures of **11** and **13** were confirmed by single-crystal X-ray diffraction technique.

Compounds **11** and **13** gave satisfactory elemental analyses. The ESI$^+$-MS mass spectra of **11**−**14** display the molecular ion (or protonated molecular ion $[M + H]^+$) or a fragmentation corresponding to the loss of Cl from the molecular ion, viz., $[M - Cl]^+$, with the characteristic isotopic distribution. The IR spectra of **11** and **13** exhibit one strong and broad ν(C≡N) peak in the 2201−2189 cm^{-1} range from both RNC ligands. The characteristic IR absorptions for the starting *cis*-$[PdCl_2(CNR^1)_2]$ complexes, usually displayed as two overlapped ν(C≡N) stretches in the 2270−2150 cm^{-1} interval, logically were not observed in the dimers. In **11**−**14**, two strong ν(C═N) bands appear between 1663 and 1565 cm^{-1}. The medium/strong-intensity bands in the 3082−2849 cm^{-1} range are characteristic of ν(C−H) vibrations, while a strong-intensity band due to δ(C−H from Ar) appears in the range 783−776 cm^{-1}.

The ^{1}H NMR spectra of **11** and **13** exhibit a set of overlapped signals in the δ 9.15−6.09 range assigned to NH_2 (for **13**) and the aromatic C−H protons. The spectra of **11** and **13** in the range δ 2.54−2.04 display four singlets due to the Me groups. In the ^{13}C NMR spectra, two overlapped signals are observed in the 194−189 ppm range for both **11** and **13**, which corresponds to the carbon resonances from C═N moieties. Signals of the Me's are observed as four singlets (19.7, 19.6, 18.7, 18.6 ppm) for **13** and two singlets (19.7, 19.5 ppm) and one broad overlapped peak (18.7 ppm) for **11**.

The crystallographic data and processing parameters for **11** and **13** are summarized in Table 3S (Supporting Information), while the corresponding plots can be found in Figure 5 and Figure 2S (Supporting Information), and bond lengths and angles are given in Table 3 and Table 4S.

In **11** and **13**, both metal centers adopt a distorted square-planar geometry. The isonitrile ligands are in *cis*-position to the C atoms of $\{\underline{C}({=}NXyl)N(Xyl)\underline{CN}(C_5H_3R^2\underline{N})\}$; the latter forms the dinuclear bicyclic framework. The bond lengths of the two coordinated CN groups in each of **11** and **13** fall in the interval of 1.144−1.153 Å, typical for the common range of the CN triple bonds in related isonitrile palladium complexes, e.g., *cis*-$[PdCl_2(CNR)_2]$ [R = Cy (1.128−1.142 Å),[51] Bu^t (1.108−1.149 Å),[52] and Xyl (1.145−1.156 Å)[53]].

In the metallacycles, the angles around the Pd centers in both **11** and **13** are within the 78.73(9)−79.36(8)° range, being slightly smaller than those previously observed in the mononuclear palladium and platinum five-membered chelates $[Pd(phen)\{\underline{C}({=}O)NPhC({=}O)\underline{N}Ph\}]$ (80.14 Å),[54] $[PdI\{\underline{C}{\equiv}NC_6H_3(2,6\text{-}Me_2)\}\{\underline{C}(C_6H_4(2\text{-}\underline{N}H_2)){=}NC_6H_3(2,6\text{-}Me_2)\}]$ (82.89 Å),[55] *cis*-$[PtCl(NH_3)(\underline{N}H_2CH_2CO\underline{O})]$ (81.56 Å),[56] and $[PtCl(PPh_3)(\underline{N}Me_2CH_2NMe_2\underline{C}H_2)](Cl)$ (82.30 Å).[57]

Among the Pd−C distances, Pd1−C6 (in **11**) and Pd1−C3 (in **13**) [1.988(2) Å] are slightly longer than (while Pd2−C24 1.977(2) Å for **11** and Pd2−C4 1.975(2) Å for **13** are equal to) those reported for the relevant palladium complexes *cis*-$[PdCl_2\{\underline{C}(OMe){=}N(H)Me\}_2]$ (1.953−1.972 Å)[48] and *cis*-$[PdCl_2\{\underline{C}({=}NHCy)NHNH\underline{C}({=}NHCy)\}_2]$ (1.958−1.964 Å).[49] The fused rings [the *first* $C^1{=}(N^1{}_{pyrNH2})N^2$Xyl group repeats the one from mononuclear **6**−**9**, while the *second* $C^2{=}(N^2Xyl)N^3$Xyl is generated during the formation of target **11**−**14**], in both complexes, are roughly planar.

In the first moiety, the bond lengths [C6−N2 1.342(3) Å and C6−N3 1.343(3) Å for **11**; C3−N3 1.346(3) Å and C3−N5 1.320(3) Å for **13**] are equal and are intermediate between the typical double and single bonds resembling the typical diaminocarbene structure. In the second fragment, the bond lengths C24−N3 1.458(3) Å (for **11**) and C4−N3 1.463(3) Å (for **13**) are single, while C24−N5 1.259(3) Å (for **11**) and C4−N4 1.257(3) Å (for **13**) are typical double bonds. All other bond lengths in **11** and **13** are normal, and their values agree with those reported for related palladium(II)[48,49,51−53] carbene and isonitrile species.

FINAL REMARKS

The results from this work may be considered from at least three perspectives. First, we discovered that metal-diaminocarbenes

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **11**

Pd(1)−Cl(1)	2.3469(5)	C(4)−C(5)	1.390(3)
Pd(1)−N(1)	2.028(2)	N(2)−C(5)	1.391(2)
Pd(1)−C(6)	1.988(2)	N(2)−C(6)	1.342(3)
Pd(1)−C(15)	1.940(2)	N(3)−C(6)	1.343(3)
Pd(2)−Cl(2)	2.4082(6)	N(3)−C(7)	1.446(3)
Pd(2)−N(2)	2.054(2)	N(3)−C(24)	1.458(3)
Pd(2)−C(24)	1.977(2)	N(4)−C(15)	1.149(3)
Pd(2)−C(33)	1.945(2)	N(4)−C(16)	1.401(3)
N(1)−C(1)	1.348(3)	N(5)−C(24)	1.259(3)
N(1)−C(5)	1.351(3)	N(5)−C(25)	1.407(3)
C(1)−C(2)	1.376(3)	N(6)−C(33)	1.153(3)
C(2)−C(3)	1.389(3)	N(6)−C(34)	1.396(3)
C(3)−C(4)	1.384(3)		
C(6)−Pd(1)−Cl(1)	172.81(6)	C(4)−C(5)−N(2)	122.9(2)
C(15)−Pd(1)−N(1)	177.25(8)	C(6)−N(2)−C(5)	115.0(2)
C(6)−Pd(1)−N(1)	79.36(8)	C(6)−N(2)−Pd(2)	114.5(1)
N(1)−Pd(1)−Cl(1)	93.97(5)	C(5)−N(2)−Pd(2)	130.1(1)
C(15)−Pd(1)−Cl(1)	86.26(6)	N(2)−C(6)−Pd(1)	115.4(1)
C(15)−Pd(1)−C(6)	100.54(8)	N(3)−C(6)−Pd(1)	130.5(2)
C(24)−Pd(2)−Cl(2)	176.99(6)	N(2)−C(6)−N(3)	114.0(2)
C(33)−Pd(2)−N(2)	174.60(8)	C(6)−N(3)−C(7)	125.5(2)
C(24)−Pd(2)−N(2)	78.90(8)	C(6)−N(3)−C(24)	117.4(2)
N(2)−Pd(2)−Cl(2)	101.47(5)	C(7)−N(3)−C(24)	117.0(2)
C(33)−Pd(2)−Cl(2)	83.44(7)	C(15)−N(4)−C(16)	175.9(2)
C(33)−Pd(2)−C(24)	96.08(9)	C(24)−N(5)−C(25)	124.1(2)
C(1)−N(1)−C(5)	119.7(2)	N(3)−C(24)−Pd(2)	110.5(1)
C(5)−N(1)−Pd(1)	113.1(1)	N(5)−C(24)−Pd(2)	135.1(2)
C(1)−N(1)−Pd(1)	126.7(1)	N(5)−C(24)−N(3)	114.4(2)
N(1)−C(5)−N(2)	116.1(2)	C(33)−N(6)−C(34)	172.0(2)
N(1)−C(5)−C(4)	120.9(2)	N(6)−C(33)−Pd(2)	171.1(2)

upon deprotonation may behave as metal-containing nucleophiles, and this property is clearly manifested in the observed coupling with ligated isonitriles leading to the unreported dimetallic species. We are currently exploring the diaminocarbene−isonitrile integration by expanding to other types of ligated aminocarbenes and to other electrophiles bearing multiple bonds. Second, the observed coupling is novel for the chemistry of coordinated isonitrile species. Indeed, previously for N-type nucleophiles, only additions of amines/hydrazines[6,11] and imines[38,39] to metal-bound isonitriles were reported. Third, the newly observed ADC−isonitrile coupling led to a dinuclear system bearing two terminal *cis*-Cl(CNR^1)[Pd] moieties, which, in turn, are expected to be employed (via similar additions) for construction of larger polymetallic species with their potential application in materials science.

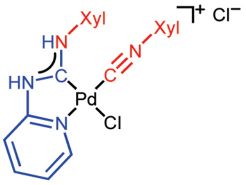
EXPERIMENTAL SECTION

Materials and Instrumentation. Solvents, all isonitriles, and pyridine-2-amine-6-R^2 were obtained from commercial sources and used as received. The complexes *cis*-[$PdCl_2(R^1NC)_2$] (R^1 = Cy and Xyl)[58−60] were prepared as previously reported. C, H, and N elemental analyses were carried out by the Department of Organic Chemistry, St.Petersburg State University. Electrospray ionization mass spectra were obtained on a Bruker microTOF spectrometer equipped with electrospray ionization (ESI) source. The instrument was operated in positive ion mode using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 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. For ESI, species were dissolved in MeCN or MeOH. In the isotopic pattern, the most intensive peak is reported. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR-8400S instrument in KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance II+ 400 MHz (UltraShield Magnet) and Bruker Avance II+ 500 MHz (UltraShield Plus Magnet) spectrometers at ambient temperature. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm relative to $SiMe_4$ (^1H and ^{13}C = 0.0 ppm) with reference to the residual solvent resonances of 7.26 ppm (^1H) and 77.1 ppm (^{13}C) for chloroform-*d*.

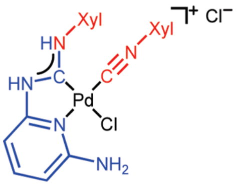
X-ray Structure Determinations. Single-crystal X-ray diffraction experiments for **6**, **6a**, **9**, **11**, and **13** were carried out with a Bruker SMART APEX II diffractometer [graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, ω-scan technique, T = 100 K (**6**, **6a**, **9**, **11**) or 150 K (**13**)]. For **6**, **6a**, **9**, and **11**, the APEX II software[61] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, and scaling and absorption correction, and SHELXTL[62] for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of NH and NH_2 groups were located in difference Fourier synthesis and refined isotropically; the rest of the hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. For **13**, cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[61] on all the observed reflections. Absorption corrections were applied using SADABS.[63] Structures were solved by direct methods by using the SHELXS-97 package[64] and refined with SHELXL-97.[62] Calculations were performed using the WinGX System, version 1.80.03.[65] All hydrogens were inserted in calculated positions. Least-square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. The principal experimental and crystallographic parameters are presented in Tables 1S and 3S of Supporting Information.

Synthetic Work. *Preparation of cis-[$PdCl_2(R^1NC)_2$] (R^1 = 2-Cl,6-MeC_6H_3) (**2**).* A mixture of solid *cis*-[$PdCl_2(MeCN)_2$] (0.259 g, 1 mmol) and 2-Cl,6-Me-C_6H_3NC (0.303 g, 2 mmol) in $CHCl_3$ (25 mL) was refluxed under vigorous stirring. After 1 h, the reaction mixture was allowed to reach room temperature and then evaporated to dryness under a stream of dinitrogen. The colorless precipitate formed was washed with three 10 mL portions of diethyl ether and dried *in vacuo* at 20−25 °C (87% isolated yield). Anal. Calcd for $C_{16}H_{12}N_2Cl_4Pd$: C 39.99; H 2.52; N 5.83. Found: C 40.11; H 2.53; N 5.49. High-resolution ESI$^+$-MS (150 V, MeCN): found 479.8768 $[M]^+$, calcd for $C_{23}H_{24}N_4ClPd$ 479.8760. ^1H NMR (CD_2Cl_2, δ): 7.40 (d, 2H, J^3_{HH} 6.5 Hz, H3), 7.39 (d, 2H, J^3_{HH} 7.5 Hz, H5), 7.30 (dd, 2H, J^3_{HH} 6.5 and 7.5 Hz, H4), 2.55 (s, 6H, Me's). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 144.1 (C1), 139.7 (C2), 131.8 (C6), 132.3 (C4), 129.7 (C5), 129.7 (C3), 19.2 (Me's).

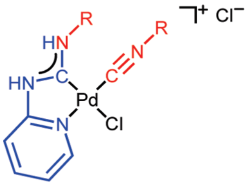
*Reaction between cis-[$PdCl_2(CNR^1)_2$] (**1**−**3**) and **4** or **5** (General Procedure).* Solid **4** or **5** (0.25 mmol) was added to a solution (for **2** and **3**) or a suspension (for **1**) (0.25 mmol) in $CHCl_3$ (5 mL), and the reaction mixture was then left to stand at 20−25 °C for 12 h. During the reaction time, the color of the mixture turned from light to lemon yellow (for **4**) or orange (for **5**). After 12 h, the reaction mixture was evaporated to dryness at 40−45 °C, whereupon the solid residue was dissolved in CH_2Cl_2 (5 mL) and filtered off from a small amount of undissolved material. The filtrate was evaporated to dryness at room temperature, washed with three 1 mL portions of Et_2O, and dried in air at 20−25 °C. Yields were 60−75%, based on Pd.



6 (75% isolated yield). Anal. Calcd for $C_{23}H_{24}N_4Cl_2Pd$: C 51.75; H 4.53; N 10.50. Found: C 51.62; H 4.42; N 10.49. High-resolution ESI$^+$-MS (150 V, MeCN): found 499.0772 $[M_{cat} - Cl]^+$, calcd for $C_{23}H_{24}N_4ClPd$ 499.0818. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3447 (m), ν(C−H) 2923 (m), ν(C≡N) 2217 (s), ν(N=$C_{carbene}$, N=C) and δ(N−H) 1628 (s), 1595 (s), 1546 (s), δ(C−H from aryls) 774 (s). ^{1}H NMR ($CDCl_3$, δ): 13.32 (s, br) and 12.14 (s, br, 2H, NH's) 9.01−8.99 (m, 1H), 7.99−7.94 (m, 1H), 7.36−7.33 (m) and 7.25−6.43 (m, 8H, aryls), 2.42 (s) and 2.19 (s, 12H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 187.8 (C=N from carbene C atom), 157.9 (C2 from the pyridine ring), 147.5, 143.0, 138.2−128.0, 118.7, 111.3 (C and CH from aryls), 19.3 and 18.5 (Me's).

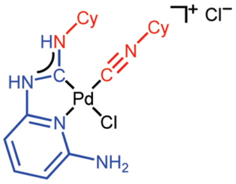


7 (72% isolated yield). Anal. Calcd for $C_{23}H_{25}N_5Cl_2Pd$: C 50.33; H 4.59; N 12.76. Found: C 50.61; H 4.87; N 12.55. High-resolution ESI$^+$-MS (70 V, MeCN): found: 514.0991 $[M_{cat} - Cl]^+$, calcd for $C_{23}H_{25}N_5ClPd$ 514.0927. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3431 (s, br), ν(C−H) 2980, 2922 (m), ν(C≡N) 2204 (s), ν(N=$C_{carbene}$, N=C) and δ(N−H) 1638, 1617 (s), 1542 (s), δ(C−H from aryls) 785 (s). ^{1}H NMR ($CDCl_3$, δ): 7.47−7.32 (m) and 7.20−6.06 (m), (m, 12H, aryls, NH's), 2.47 (s), 2.21 (s, 12H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 185.5 (C=N from carbene C atom), 158.9 (C2 from the pyridine ring), 154.5 (C6 from the pyridine ring), 143.0, 134.2−127.2, 116.7, 111.3 (C and CH from aryls), 19.2 and 18.4 (Me's).

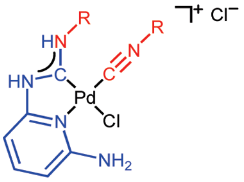


R = 2-Cl-6-Me-C_6H_3

8 (62% isolated yield). Anal. Calcd for $C_{21}H_{18}N_4Cl_4Pd$: C 43.89; H 3.15; N 9.75. Found: C 44.17; H 3.38; N 9.54. High-resolution ESI$^+$-MS (70 V, CH_2Cl_2): found 538.9531 $[M_{cat} - Cl]^+$, calcd for $C_{21}H_{18}N_4Cl_3Pd$ 538.9726. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3445 (s, br), ν(C−H) 2949 (m), 2838 (m), ν(C≡N) 2208 (s), ν(N=$C_{carbene}$, N=C) and δ(N−H) 1639, 1620 (s), 1549 (s), δ(C−H from aryls) 772 (s). ^{1}H NMR ($CDCl_3$, δ): 13.46 (s, br), 12.35 (s, br, 2H, NH's) 9.03−9.00 (m), 8.02−7.96 (m), 7.39−7.30 (m), and 7.23−6.87 (m, 10H, aryls), 2.51 (s), 2.32 (s, 6H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 195.3 (C=N from carbene C atom), 155.8 (C2 from the pyridine ring), 166.6, 140.8, 136.9, 130.9, 129.3, 127.8, 127.6, 113.8, 113.4, 112.1, 111.8 (C and CH from aryls), 19.5 and 18.3 (Me's).



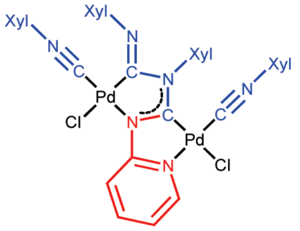
9 (60% isolated yield). Anal. Calcd for $C_{19}H_{28}N_5ClPd \cdot CHCl_3$: C 40.87; H 4.97; N 11.91. Found: C 41.12; H 5.21; N 11.83; solvated $CHCl_3$ molecule has been detected in the NMR spectra measured in DMSO-d_6. High-resolution ESI$^+$-MS (70 V, MeOH): found 470.1129 $[M_{cat}]^+$, calcd for $C_{19}H_{28}N_5ClPd$ 470.1162. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3323 (m), ν(C−H) 3172 (m), 2933 (s), 2857 (s), ν(C≡N) 2239 (s), ν(N=$C_{carbene}$, N=C) and δ(N−H) 1653 (s), 1624 (s), 1589 (s), 1568 (s), δ(C−H from the pyridine ring) 780 (s). ^{1}H NMR (DMSO-d_6, δ): 8.62 (s, 2H, NHs), 7.96 (s, 2H, NH_2), 7.53 (t, J^3_{HH} 8.0 Hz, 1H, H4 from the pyridine ring), 6.71 (d, J^3_{HH} 7.5 Hz, 1H), 6.29 (d, J^3_{HH} 8.5 Hz, 1H, H3+H5 from the pyridine ring), 4.29 (m) and 4.21 (m, 2H, CH), 1.86−1.08 (m, 20H, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 172.2 (C=N from carbene C atom), 161.8, 152.5 (C2 + C6 from the pyridine ring), 141.9 (C4), 106.0 (C5), 97.6 (C3 from the pyridine ring), 55.3, 54.8 (CH from Cy's), 31.8, 31.0, 25.1, 24.8, 24.7, 22.2 (CH_2).



R = 2-Cl-6-Me-C_6H_3

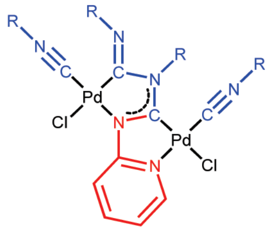
10. High-resolution ESI$^+$-MS (70 V, MeCN): found 553.9917 $[M_{cat} - Cl]^+$, calcd for $C_{21}H_{19}N_5Cl_3Pd$ 553.9835. The reaction between **2** and **5** led to formation of a dark orange, oily residue, which was a broad mixture of products (five spots on TLC). High-resolution ESI$^+$-MS showed the presence of **10** and dinuclear **14** among the other products.

*Reaction of **1** or **2** with **6**−**8** and **10** (General Procedure).* Each of solid **6**−**8** or **10** (0.25 mmol) was added to a solution (for **2**) or a suspension (for **1**) (0.25 mmol) in $CHCl_3$ (5 mL), and the reaction mixture was stirred with an excess of K_2CO_3 (1.50 mmol) at 40 °C for 12 h. During the reaction time, the mixture turned from colorless to lemon yellow (for **6** and **7**) or orange (for **8** and **10**). After 12 h, the reaction mixture was filtered off from the solid material and evaporated to dryness at 40−45 °C, whereupon the oily residue formed was dissolved in CH_2Cl_2 (5 mL). The filtrate was evaporated to dryness at room temperature, washed with three 1 mL portions of Et_2O, and dried in air at 20−25 °C. Yields were 65−75%, based on Pd.



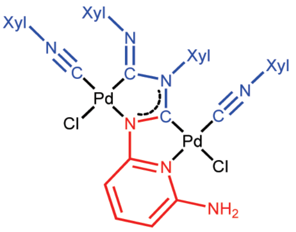
11 (75% isolated yield). Anal. Calcd for $C_{41}H_{40}N_6Cl_2Pd_2$: C 54.68; H 4.47; N 9.33. Found: C 54.75; H 4.56; N 9.46. High-resolution ESI$^+$-MS

(150 V, MeCN): found 902.0426 [M + H]$^+$, calcd for $C_{41}H_{40}N_6Cl_2Pd_2$ 902.0955. IR (KBr, selected bands, cm^{-1}): ν(C−H) 3081 (m), 2919 (s), 2849 (s), ν(C≡N) 2201 (s), ν(N═C) 1663 (s), 1608 (s), δ(C−H from aryls) 777 (s). ^{1}H NMR ($CDCl_3$, δ): 9.06−8.99 (m, 1H), 7.87−7.82 (m, 1H), 7.22−6.17 (m, 14H, aryls), 2.45 (s, 6H), 2.27 (s, 6H), 2.23 (s, 6H), 2.04 (s, 6H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 194.8 and 167.0 (C═N), 162.5, 149.5, 147.6, 146.9, 143.0, 141.8, 136.8−134.3, 129.8−126.7, 123.8, 118.5, 117.5 (C and CH from aryls), 19.7, 19.5, 18.7 (Me's).

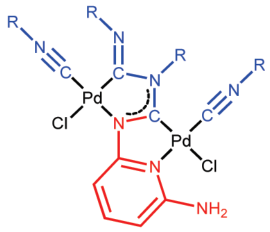


R = 2-Cl-6-Me-C_6H_3

12. High-resolution ESI$^+$-MS (70 V, MeCN): found 946.8987 [M − Cl]$^+$, calcd for $C_{37}H_{28}N_6Cl_5Pd_2$ 946.8862. The reaction between **2** and **7** led to formation of an orange, oily residue of a broad mixture of products. High-resolution ESI$^+$-MS showed the presence of **12** among other species.



13 (65% isolated yield). Anal. Calcd for $C_{41}H_{41}N_7Cl_2Pd_2 \cdot CH_2Cl_2$: C 50.42; H 4.33; N 9.79. Found: C 50.57; H 4.41; N 9.62; solvated CH_2Cl_2 molecule has been detected in the NMR spectra measured in $CDCl_3$. High-resolution ESI$^+$-MS (70 V, MeOH): found 880.1204 [M − Cl]$^+$, calcd for $C_{41}H_{41}N_7ClPd_2$ 880.1297. IR (KBr, selected bands, cm^{-1}): ν(N−H) 3237 (m), ν(C−H) 2915 (s), 2851 (s), ν(C≡N) 2190 (s), ν(N═C) 1638 (s), 1565 (s), δ(C−H from aryls) 783 (s). ^{1}H NMR ($CDCl_3$, δ): 8.04 (d), 7.46−7.30 (m), 7.21−6.86 (m), 6.65−6.09 (m, 15H, aryls), 6.80 (s, 2H, NH_2), 2.50 (s, 6H), 2.28 (s, 6H), 2.24 (s, 6H), 2.05 (s, 6H, Me's). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 189.3 and 163.0 (C═N), 162.9, 160.9, 149.3, 142.6−123.5, 105.4 (C and CH from aryls), 19.7, 19.6, 18.7, 18.6 (Me's).



R = 2-Cl-6-Me-C_6H_3

14. High-resolution ESI$^+$-MS (70 V, MeCN): found 997.8428 [M]$^+$, calcd for $C_{37}H_{29}N_7Cl_6Pd_2$ 997.8801. The reaction between **2** and **5** led to the formation of a dark orange, oily residue of a broad mixture of products (five spots on TLC). High-resolution ESI$^+$-MS indicated the presence of **10** and dinuclear **14** among other species.

■ ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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