

**Palladium(II)-mediated Addition of Benzenediamines to Isocyanides. Generation of Three Types of Diaminocarbene Ligands Depending on Isomeric Structure of the Nucleophile**

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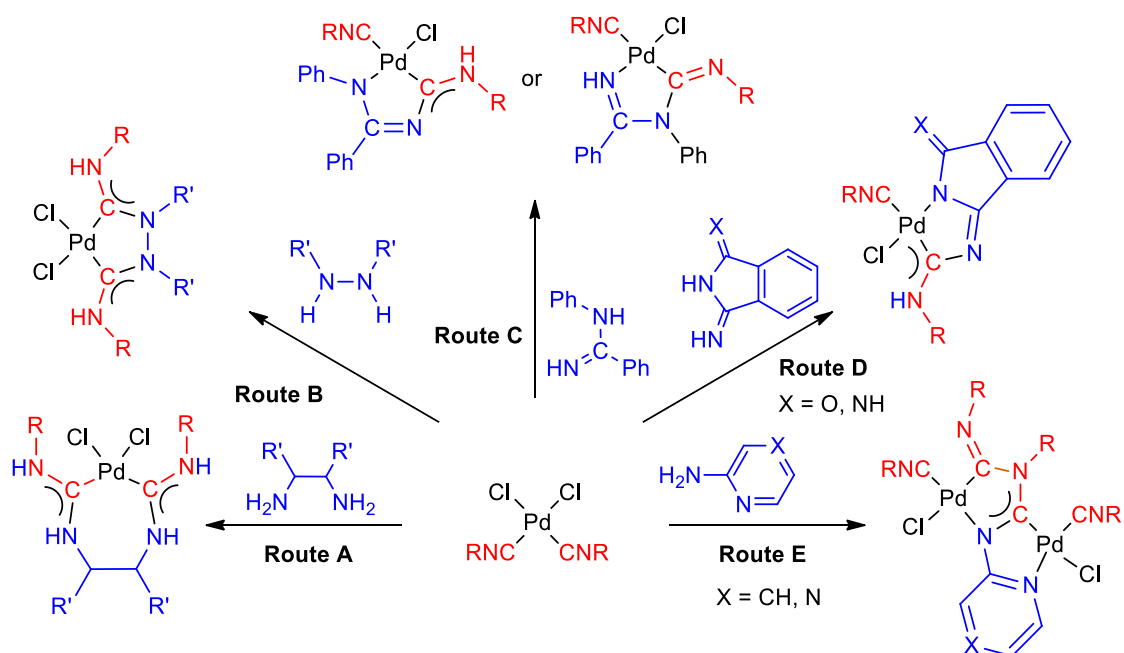
## Abstract

Coupling of the palladium-*bis*(isocyanide) complexes *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>] (R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **1**, 2-Cl-6-MeC<sub>6</sub>H<sub>3</sub> **2**) with benzene-1,3-diamine (**BDA1**) leads to the diaminocarbene species *cis*-[PdCl<sub>2</sub>(CNR){C(NHR)=NH(1,3-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)}] (**5** and **6**, respectively). In this reaction, **BDA1** behaves as a monofunctional nucleophile that adds to one of the RNC ligands by one amino group. By contrast, reaction of **1** and **2** with benzene-1,4-diamine (**BDA2**) involves both amino functionalities of the diamine and leads to the binuclear species [*cis*-PdCl<sub>2</sub>(CNR){ $\mu$ -C(NHR)=NH(1,4-C<sub>6</sub>H<sub>4</sub>)NH=C(NHR)}-(*cis*)-PdCl<sub>2</sub>(CNR)] (**6** and **7**) featuring two 1,4-bifunctional diaminocarbene ligands. Reaction of *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>] (R = cyclohexyl **3**) with either **BDA1** or **BDA2** does not afford any isolable carbene derivatives. The most versatile chemistry was observed when **1–3** were treated with benzene-1,2-diamine (**BDA3**) and the relevant substituted 1,2-diamines, viz., 4,5-dimethylbenzene-1,2-diamine (**BDA4**) and 4,5-dichlorobenzene-1,2-diamine (**BDA5**). Addition of these diamines brings about the formation of the monocarbene cationic complexes *cis*-[PdCl(CNR){C(NHR)=NHC<sub>6</sub>H<sub>2</sub>X<sub>2</sub>NH<sub>2</sub>}]Cl (X = H, Me, Cl) (**8–16**), the Chugaev-type *C,C*-bound *bis*-carbenes *cis*-[PdCl<sub>2</sub>{C(NHR)=NHC<sub>6</sub>H<sub>2</sub>X<sub>2</sub>NH=C(NHR)}] (**17**, **18**), and the *bis*(*C,N*-chelated)carbene complexes *cis*-[Pd{C(NHR)=NHC<sub>6</sub>H<sub>2</sub>X<sub>2</sub>NH<sub>2</sub>}<sub>2</sub>]Cl<sub>2</sub> (**19–24**). All prepared complexes (with an exception of **17** and **18**) were isolated as colorless or pale yellow solids and characterized by elemental analyses (C, H, N), HRESI<sup>+/-</sup>-MS, IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies, and **4**, **7**, **13**, **16**, and **24** by X-ray diffraction. Complexes **17** and **18** were characterized by HRESI<sup>+/-</sup>-MS, IR spectroscopy, and their structures were established by X-ray crystallography.

## Introduction

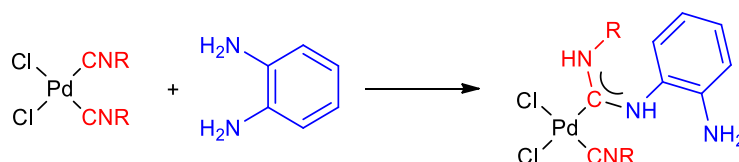
Metal-mediated addition of *N*-nucleophiles to coordinated isocyanides is known to afford complexes bearing acyclic diaminocarbene ligands (M-ADCs).<sup>1-4</sup> These species are recognized as efficient organometallic catalysts,<sup>5-13</sup> with corresponding palladium derivatives demonstrating outstanding performance in cross-coupling processes,<sup>5,6,10,11</sup> whereas platinum-ADCs are efficient in hydrosilylation of alkenes.<sup>8</sup>

The vast majority of known palladium-ADC species are monodentate and are generated through nucleophilic addition of monofunctional *N*-nucleophiles (e.g. amines) to metal-bound CNR ligands.<sup>1-3</sup> The addition of bifunctional *N,N*-nucleophiles is so far limited to few examples.<sup>4</sup> Thus, the interplay between *bis*-isocyanide palladium(II) complexes and aliphatic 1,2-diamines proceeds via the attack by both amino groups on two CNR ligands leading to *C,C*-chelated *bis*-carbene derivatives (**Scheme 1, Route A**).<sup>14,15</sup> Closely related addition of aliphatic hydrazines brings about the formation of the Chugaev-type<sup>4</sup> *C,C*-bound *bis*-carbenes (**Route B**).<sup>16,17</sup> Coupling of palladium *bis*-isocyanides with ambident *N*-phenylbenzamidines proceeds regioselectively to afford *C,N*-chelated species, and the regioselectivity is controlled by the nature of R in RNCs (**Route C**).<sup>18</sup> Reaction of palladium-CNRs with such heterocyclic imines as 1,3-diiminoisoindolines and 3-iminoisoindolin-1-ones produces *C,N*-chelated diaminocarbenes (**Route D**).<sup>19-21</sup> Finally, the reaction of (RNC)Pd<sup>II</sup> species with aminopyridines leads to the binuclear complexes containing bridging aminocarbene ligand; this reaction proceeds through the intermediate generation of the mononuclear carbene species that further attacks the starting palladium-isocyanide complex (**Route E**).<sup>22,23</sup>



**Scheme 1.** Coupling of isocyanides in  $cis$ -[PdCl<sub>2</sub>(CNR)<sub>2</sub>] with various ambident nucleophiles.

Although regioselectivity of the addition of bifunctional reagents to RNC ligands was studied, the effect of the isomeric composition of polyfunctional nucleophiles on structure of the product formed has never been investigated. Thus, while in the case of benzene-1,*n*-diamines (*n* = 2–4), Belluco and co-workers reported<sup>24</sup> the reaction of benzene-1,2-diamine with a coordinated isocyanide in  $cis$ -[PdCl<sub>2</sub>(CNPh)<sub>2</sub>] leading to the conventional monodentate Pd-ADC complex  $cis$ -[PdCl<sub>2</sub>(CNPh){C(NHPh)=NH(1,2-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)}] (**Scheme 2**), no reaction with the isomeric benzene-1,3- and 1,4-diamines was studied.



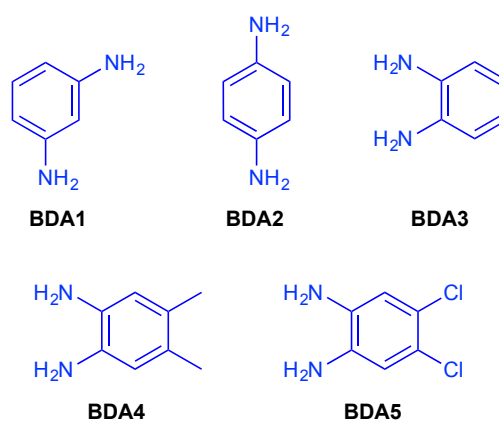
**Scheme 2.** The reported addition of benzene-1,2-diamine to Pd<sup>II</sup>-bound isocyanides.<sup>24</sup>

In the framework of our projects on metal-involving reactions of RNCs<sup>1,4,10,11,18,19,21-23,25-27</sup> and catalytic activity of (ADC)M systems,<sup>5,8,10,11,20,21,28,29</sup> we undertook a systematic study aimed

at recognition of the influence of isomeric composition of aromatic benzene-1,*n*-diamines (*n* = 2–4) on the structure of the carbene product formed upon reaction with palladium-bound isocyanides. We observed that isomeric composition strongly affects the nature of ADC formed and our results are disclosed in the sections that follow.

## Results and Discussion

For this study, we addressed, on the one hand, the known palladium-isocyanide complexes *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>] [R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (Xyl) **1**, 2-Cl-6-MeC<sub>6</sub>H<sub>3</sub> **2**, cyclohexyl (Cy) **3**]<sup>22,30</sup> and, on the other hand, the isomeric benzene-1,*n*-diamines (**Figure 1**), *i.e.*, benzene-1,3-diamine (**BDA1**), benzene-1,4-diamine (**BDA2**), and benzene-1,2-diamine (**BDA3**). In addition, substituted 1,2-diamines such as 4,5-dimethylbenzene-1,2-diamine (**BDA4**) and 4,5-dichlorobenzene-1,2-diamine (**BDA5**) were employed as reactants.

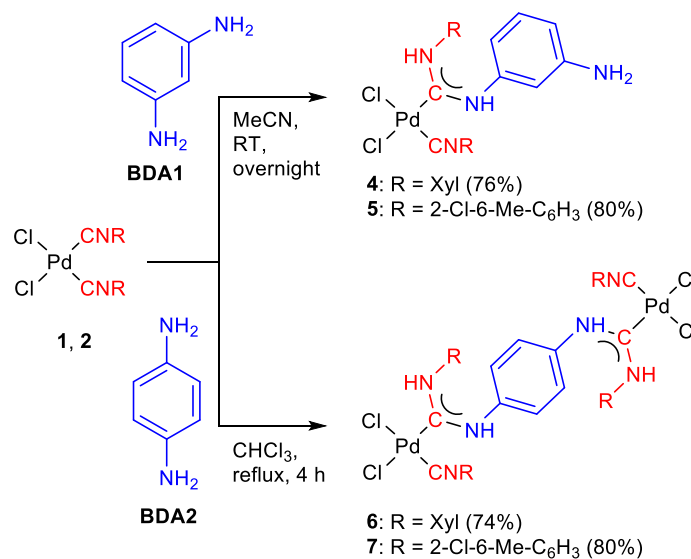


**Figure 1.** Isomeric benzene-1,*n*-diamines **BDA1–BDA5**.

(i) *Reactions of palladium-isocyanide complexes 1–3 with benzene-1,3-diamine (BDA1).*

Owing to the absence of conjugation between the two amino groups, benzene-1,3-diamine **BDA1** among the isomeric benzene-1,*n*-diamines is the most related to aniline. Consequently, the reaction of **BDA1** and complexes **1** (or **2**) in a molar ratio 1:1 (RT, MeCN, overnight) affords

typical monodentate diaminocarbene palladium species **4** or **5** (76–80%; **Scheme 3**) and these results agree with those reported by Belluco et al. for benzene-1,2-diamine.<sup>24</sup> The products were separated by filtration and HRESI<sup>+/-</sup>-MS monitoring of the dark filtrate indicated the absence of any other palladium complexes apart from **4** or **5** that exist in the mixture with some organic species.



**Scheme 3.** Reactions of **1** and **2** with **BDA1** and **BDA2**.

In agreement with the IR and NMR data (see Experimental) both **4** and **5** possess pendant unprotonated amino group. We attempted to involve both amino group of **BDA1** in the reaction with RNC ligand by refluxing a mixture of complex **1** (**2**) with **BDA1** in molar ratios 1:1 and 2:1 in MeCN (4 h) or CHCl<sub>3</sub> (4 h). Monitoring of the reaction mixture by HRESI<sup>+/-</sup>-MS indicated the presence of palladium complex of **4** (**5**) and [PdCl(CNR){C(NHR)=NH(1,3-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)}{1,3-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>}]<sup>+</sup> along with a broad range of yet unidentified Pd species. Our attempts to isolate any pure palladium compound from these reaction mixtures were unsuccessful.

Furthermore, treatment of one equiv of *bis*(isocyanide) complex **1** with **4** (or *bis*(isocyanide) complex **2** with **5**) does not lead to the coupling of the unreacted amino group with the RNC ligands either. All these observations indicate that the nucleophilic addition of one amino

group of **BDA1** onto Pd<sup>II</sup>-activated RNC reduces the nucleophilicity of the pendant NH<sub>2</sub>-moiety and it loses its reactivity toward the isocyanide ligands. It is noteworthy, that the reaction of complex **3** with **BDA1** even at RT yielded a mixture of yet unidentified products along with traces of metallic Pd.

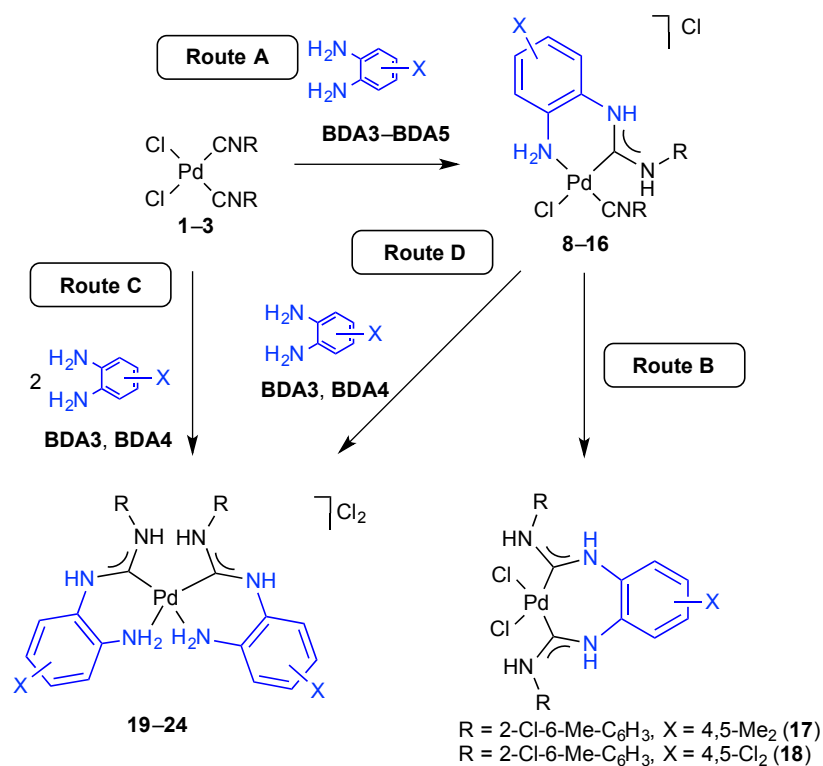
(ii) *Coupling of palladium-isocyanide complexes 1–3 with benzene-1,4-diamine (BDA2).*

The reaction between benzene-1,4-diamine (**BDA2**) and any one of **1–3** in an MeCN solution at RT yielded Pd black and no pure palladium complex was isolated from those reaction mixtures. Monitoring of these mixtures by HRESI<sup>+/-</sup>-MS indicated the presence of [PdCl(CNR){C(NHR)=NH(1,4-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)}]<sup>+</sup>, [PdCl(CNR){C(NHR)=NH(1,4-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)}(1,4-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>)]<sup>+</sup> ions, and some unidentified Pd complexes. However, reflux of complexes **1** or **2** and **BDA2** in a molar ratio 1:1 in CHCl<sub>3</sub> instead of MeCN for 4 h led to formation of binuclear species **6** or **7**, where both amino groups are involved in generation of the carbene moieties (**Scheme 3**); approximately a half of the starting diamine remains unreacted as verified by <sup>1</sup>H NMR. The reaction of *bis*(isocyanide) complexes **1** or **2** with **BDA2** in a molar ratio 2:1 (CHCl<sub>3</sub>, reflux, 4 h) afforded **6** or **7** in good yields (74% and 80%, respectively), which were separated by filtration after cooling the reaction mixture to RT. We believe that the reason for the difference in reactivity between the 1,3- and 1,4-diamines is due to the higher nucleophilicity of benzene-1,4-diamine.<sup>31</sup> Noticeably, complex **3** is reduced to Pd black by diamine **BDA2** in a CHCl<sub>3</sub> solution.

(iii) *Coupling of palladium-isocyanide complexes 1–3 with 1,2-diamines BDA3–BDA5.*

The reaction of **1–3** and **BDA3–BDA5** (molar ratio 1:1, CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>, RT, overnight) in all possible combinations gave monocationic aminocarbene complexes **8–16** in 69–82% isolated yields (**Route A, Scheme 4**; see **Table 1** for compound numbering). Based on the X-ray data, in **8–16**, the aminocarbene ligands are coordinated to the metal centers in a bidentate mode, *i.e.* through the carbene carbon and via the second amine group of the 1,2-diamine moiety thus leading to the *C,N*-coordination. The close similarities of the IR spectra of **8–16** in the solid state (either in Nujol or in KBr) and in a solution (CHCl<sub>3</sub>) indicate that **8–16** in the solution also exist in

the chelated form. This coordination mode was previously reported for the range of ambident nucleophiles (**Scheme 2**, products of **C–E**).<sup>4</sup>



**Scheme 4.** Nucleophilic additions of 1,2-diamines **BDA3–BDA5** to the isocyanides in **1–3**.

**Table 1.** Numbering for the compounds **8–16** and **19–24** (for the latter given in parentheses).

Benzene-1, <i>n</i> -diamine used	R in starting complex <i>cis</i> -[PdCl <sub>2</sub> (CNR) <sub>2</sub> ]		
	Cy	Xyl	2-Cl-6-MeC <sub>6</sub> H <sub>3</sub>
<b>BDA3</b> (X = H)	<b>8 (19)</b>	<b>9 (20)</b>	<b>10 (21)</b>
<b>BDA4</b> (X = 4,5-Me <sub>2</sub> )	<b>11 (22)</b>	<b>12 (23)</b>	<b>13 (24)</b>
<b>BDA5</b> (X = 4,5-Cl <sub>2</sub> )	<b>14 (–)</b>	<b>15 (–)</b>	<b>16 (–)</b>

Complexes **8–16** are stable upon reflux in CHCl<sub>3</sub> or MeCN for ca. 24 h. However, after 2 months at RT a small amount of crystalline material (**17** and **18**; **Scheme 4**, **Route B**) was released from solutions of **13** and **16**, correspondingly. These crystals were mechanically separated and



characterized by IR spectroscopy and X-ray diffraction indicating that **17** and **18** are the Chugaev-type<sup>4</sup> *C,C*-chelated *bis*-carbene derivatives.

We believe that appearance of **17** and **18** in the system is the result of the palladium(II)-mediated intramolecular nucleophilic addition of the pendant amine moiety to the CNR ligand in **13** and **16** that occurs similarly to other reported insertions of ambident nucleophiles (see **Section 2.4** of our review<sup>4</sup>). However, all attempts to develop high yielding synthetic routes to **17** and **18** by either treatment of **13** and **16** with the corresponding CNRs or by treatment of **13** and **16** with excess (*n*-Bu<sub>4</sub>N)Cl were not successful. If in the former case we obtained broad mixtures with no **17** and **18**, in the latter case no reaction was observed.

Addition of 2 equiv **BDA3** or **BDA4** to a suspension (for **1** and **2**) or a solution (for **3**) of one equiv the corresponding isocyanide complex (MeCN, RT) led to a rapid precipitation of *bis*-carbenes **19–24** (**Scheme 4, Route C; Table 1**) except for the reaction between **3** and **BDA4** that proceeded for ca. 2 h only at 70 °C. Complexes **19–24** were also obtained by the reaction of **8–13** with **BDA3** or **BDA4** (a molar ratio 1:1) in MeCN (80–93%) (**Scheme 4, Route D**). The reactions of **BDA5** with any one of **1–3** (a molar ratio 2:1) furnished only corresponding monocarbene products **14–26** (via **Route B**) and no *bis*(*C,N*-chelated)carbene complexes were detected in the reaction mixture even after reflux of **1–3** (1 equiv) in an MeCN solution in the presence of large excess of **BDA5** (4 equiv) for 24 h.

It should be mentioned that the lower reactivity of the second isocyanide ligand toward the nucleophilic addition is commonly observed for *bis*-isocyanide metal species, e.g. *cis*-[PdCl<sub>2</sub>(CNR)<sub>2</sub>]. A possible rationale for this behavior is that the carbene ligand formed, being a stronger donor compared to the isocyanide, deactivates the second CNR ligand toward the nucleophilic addition.<sup>5</sup> In this study, we found that the reaction of palladium *bis*-isocyanides with 1,2-diaminobenzenes proceeds at both isocyanide ligands and, most likely, the chelation drives the second addition.

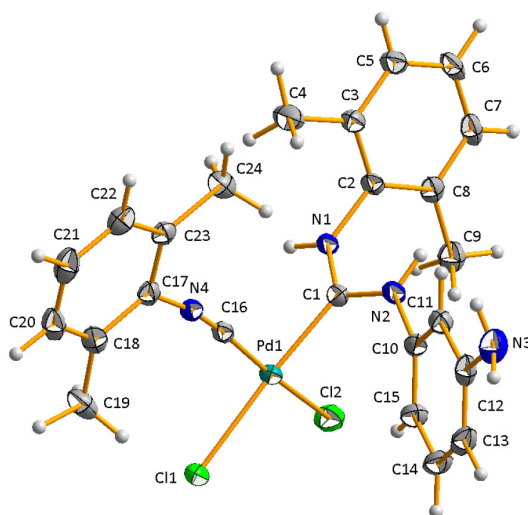
**Characterization of the aminocarbene complexes.** Complexes **4–16** and **19–24** were obtained as colourless or pale yellow solids and characterized by elemental analyses (C, H, N), HRESI<sup>+/-</sup>-MS, IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopies. In addition, the structures of **4**, **7**, **13**, **16**, and **24** were elucidated by single-crystal X-ray diffraction studies. Complexes **17** and **18** were characterized by IR spectroscopy, HRESI<sup>+/-</sup>-MS, and their structures were determined by X-ray crystallography.

Complexes **4–16** and **19–24** gave satisfactory CHN-microanalyses that are consistent with the proposed formulas. In the HRESI<sup>+</sup>-MS of **4–16** and **19–24**, ions [M–Cl]<sup>+</sup> and/or [M–2Cl–H]<sup>+</sup> with the characteristic isotopic distribution were detected. In addition, the *m/2* peaks from [M–2Cl]<sup>2+</sup> were observed in the mass spectra of **6** and **7**. The HRESI<sup>-</sup>-MS of **5**, **12**, and **22–24** display ion peaks [M–H]<sup>-</sup> and/or [M–Cl–2H]<sup>-</sup>. The IR spectra of **4–24** indicated formation of the carbene moiety, thus, intense absorption at 1570–1545 cm<sup>-1</sup> was assigned to  $\nu(\text{N}-\text{C}_{\text{carbene}})$  and corresponding  $\nu(\text{N}-\text{H})$  bands emerge in the range of 3250–3040 cm<sup>-1</sup>, whereas  $\delta(\text{N}-\text{H})$  is closer to 1500 cm<sup>-1</sup>. The IR spectra of **4–16** display one strong  $\nu(\text{C}\equiv\text{N})$  stretching vibration in the range between 2240 and 2198 cm<sup>-1</sup> belonging to one unreacted isocyanide ligand, whereas starting complexes **1–3** display two overlapped  $\nu(\text{C}\equiv\text{N})$  bands in the interval 2265–2208 cm<sup>-1</sup>.<sup>22,30,32,33</sup> The IR spectra of **17–24** display no bands in the range between 2300 and 2190 cm<sup>-1</sup> corresponding to  $\nu(\text{C}\equiv\text{N})$ , thus supporting the transformation of both isocyanide ligands into aminocarbenes.

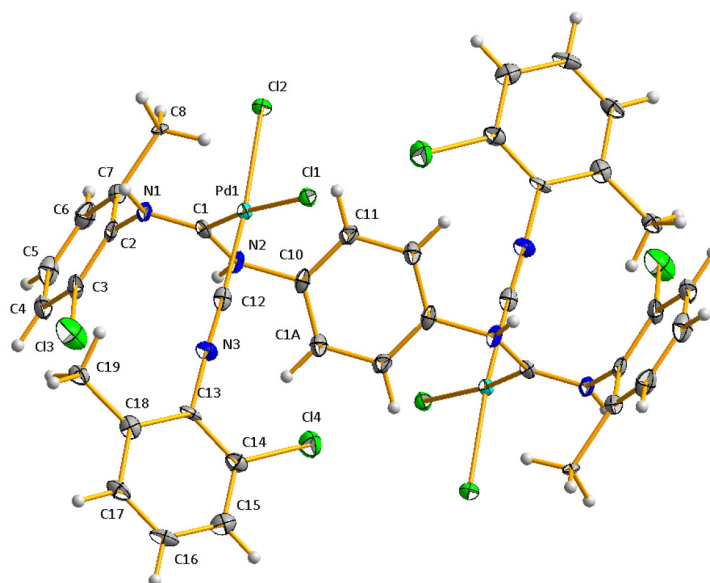
The <sup>13</sup>C{<sup>1</sup>H} NMR data also confirmed the structures of the synthesized species. Addition of **BDA1–BDA5** to **1–3** is accompanied by a pronounced downfield  $\delta$  <sup>13</sup>C shift of one or both of the isocyanide quaternary C atom to the range that is specific for ADC Pd–C<sub>carbene</sub> ( $\delta_{\text{C}}$  160–224 ppm).<sup>11,15,19,22,34</sup> The C<sub>carbene</sub>=NH <sup>13</sup>C signals in **4–16** were found to resonate in the range of  $\delta_{\text{C}}$  173–184 ppm, that is *ca.* 70 ppm downfield shifted *vs.* **1** (*e.g.*  $\delta_{\text{C}}$  115 ppm for C≡N). These  $\delta$  values for the C<sub>carbene</sub>=NH <sup>13</sup>C signal are upfield relatively to those ( $\delta_{\text{C}}$  197–201 ppm) reported for the series of palladium complexes bearing the chelating acyclic aminocarbene ligands [PdCl{C(N=C(C<sub>6</sub>R<sup>2</sup>R<sup>3</sup>R<sup>4</sup>R<sup>5</sup>CON))=N(H)R<sup>1</sup>}(CNR<sup>1</sup>)].<sup>19</sup> In the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **19–24**,

the  $C_{\text{carbene}}\text{-NH}$  signals were found to resonate in the range of  $\delta_{\text{C}}$  183–188 ppm, which is slightly (5–10 ppm) downfield from the signals of monocarbene complexes **4**–**16**.

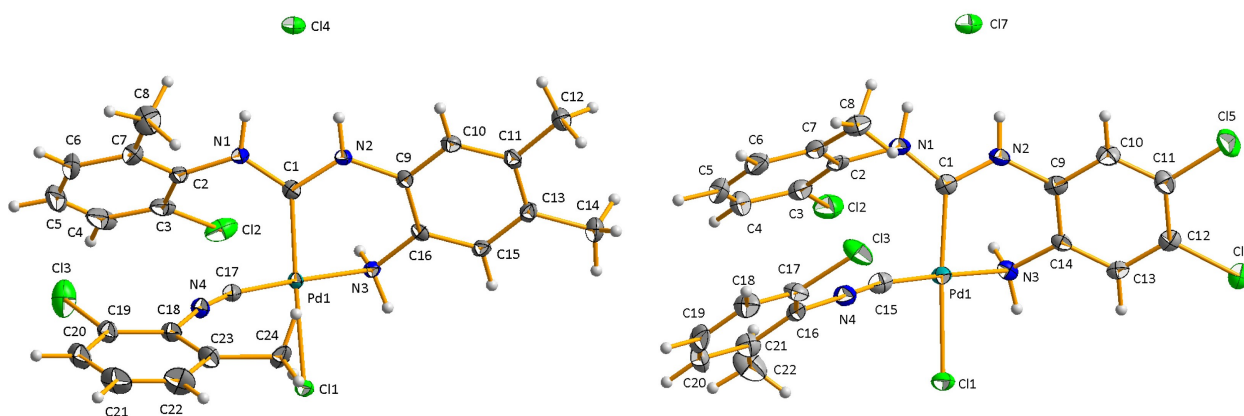
The crystallographic data and processing parameters for **4**, **7**, **13**, **16**–**18**, and **24** are listed in **Table S1 (Supplementary Information)**; the plots for the structures can be found in **Figures 2**–**6**.



**Figure 2.** View of **4** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity. Selected bond lengths (Å) and angles (°): Pd1–C16 1.929(3) Pd1–C1 1.979(3); Pd1–Cl2 2.3289(8); Pd1–Cl1 2.3843(7); N1–C1 1.320(3); N1–C2 1.446(3); N2–C1 1.329(4); N2–C10 1.440(3); N3–C12 1.388(4); N4–C16 1.156(4); N4–C17 1.405(4); C16–Pd1–C1 90.49(11); C16–Pd1–Cl2 175.94(8); C1–Pd1–Cl2 86.49(8); C16–Pd1–Cl1 89.84(8); C1–Pd1–Cl1 175.53(8); Cl2–Pd1–Cl1 93.39(3); C1–N1–C2 125.7(2); C1–N2–C10 126.3(2); C16–N4–C17 171.5(3); N1–C1–N2 118.0(3); N1–C1–Pd1 119.6(2); N2–C1–Pd1 122.3(2); N4–C16–Pd1 175.9(2).

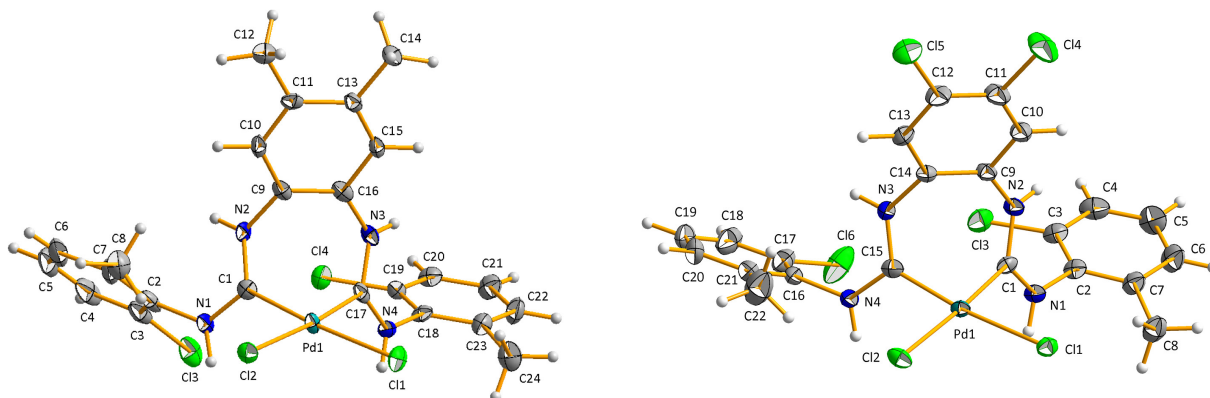


**Figure 3.** View of **7** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity. Selected bond lengths (Å) and angles (°): Pd1–C12 1.935(6); Pd1–C1 1.974(5); N3–C12 1.159(7); N3–C(13) 1.385(7); N2–C1 1.326(6); N2–C(10) 1.432(6); N1–C1 1.312(6); N1–C2 1.443(7); C12–Pd1–C1 86.8(2); C1–N1–C2 122.9(4); N1–C1–N2 119.3(5); C12–N3–C(13) 176.1(5); N3–C12–Pd1 176.0(4); N2–C1–Pd1 118.2(4); N1–C1–Pd1 122.5(4).

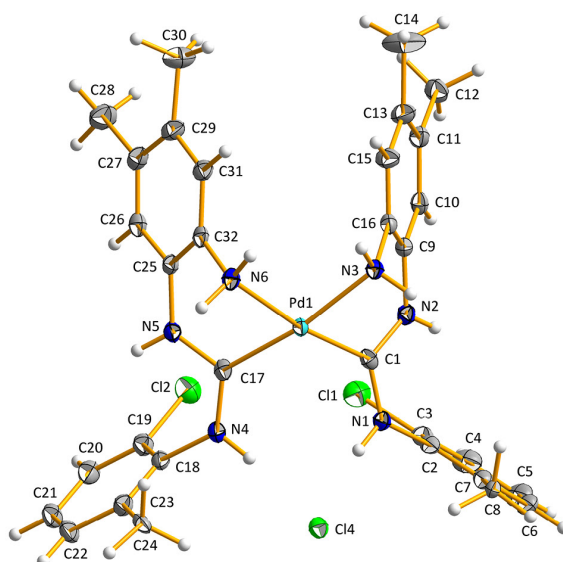


**Figure 4.** View of **13** (left) and **16** (right) with the atomic numbering schemes. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity. Selected bond lengths (Å) and angles (°) for **13**: Pd1–C17 1.942(3); Pd1–C1 1.974(3); Pd1–N3 2.063(2); Pd1–Cl11 2.3439(7); N1–C1 1.339(3); N1–C2 1.419(3); N2–C1 1.332(3); N2–C(9) 1.418(3); N4–C17 1.152(4); N4–C18 1.397(4); C17–Pd1–C1 94.32(11); C1–Pd1–N3 86.80(10); N2–C1–N1

114.4(2); C17–N4–C18 169.4(3). Selected bond lengths (Å) and angles (°) for **16**: Pd1–C15 1.950(7); Pd1–C1 1.998(6); Pd1–N3 2.061(5); Pd1–Cl1 2.3315(16); Pd1–C15B 1.942(7); Pd1–C1 2.003(6); Pd1–N3B 2.052(5); Pd1–Cl1 2.3264(15); N2–C1 1.331(7); N1–C1 1.334(7); N4–C15 1.143(8); N4–C16 1.398(8); C15–Pd1–C1 96.4(2); C15–Pd1–N3 177.7(2); C1–Pd1–N3 85.2(2); N2–C1–N1 113.9(5); C15–N4–C16 172.6(6).



**Figure 5.** View of **17** (left) and **18** (right) with the atomic numbering schemes. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity Selected bond lengths (Å) and angles (°) for **17**: Pd1–C1 1.961(7); Pd1–C17 1.974(7); Pd1–Cl2 2.3742(18); Pd1–Cl1 2.3777(18); Pd1–C1 1.961(7); Pd1–C17B 1.970(7); Pd1–Cl1 2.3693(19); Pd1–Cl2B 2.3778(18); N3–C17 1.333(9); N4–C17 1.306(9); N4–C18 1.427(9); N2–C1 1.324(9); N1–C1 1.336(9); N1–C2 1.459(9); C1–Pd1–C17 84.7(3); Cl2–Pd1–Cl1 94.09(7); C1–Pd1–C17B 86.3(3); Cl1–Pd1–Cl2B 92.50(7); N4–C17–N3 119.2(6); C17–N4–C18 126.2(6); C1–N1–C2 124.4(6); N2–C1–N1 118.3(6); and for **18**: Pd1–C1 1.960(3); Pd1–C15 1.958(3); Pd1–Cl2 2.3683(9); Pd1–Cl1 2.3755(8); N1–C1 1.319(4); N2–C1 1.338(4); N3–C15 1.334(4); N4–C15 1.326(4); C15–Pd1–C1 86.82(13); Cl2–Pd1–Cl1 93.24(3); N1–C1–N2 119.2(3); N4–C15–N3 118.1(3).



**Figure 6.** View of **24** with the atomic numbering scheme. Thermal ellipsoids are drawn with the 50% probability. Hydrogen labels are omitted for simplicity. Selected bond lengths (Å) and angles (°): Pd1–C1 2.008(3); Pd1–C17 2.027(3); Pd1–N3 2.095(2); Pd1–N(6) 2.105(2); N3–C16 1.438(4); N1–C1 1.329(4); N1–C2 1.434(4); N2–C1 1.332(4); N2–C(9) 1.420(4); N4–C17 1.331(4); N4–C18 1.443(4); N5–C17 1.333(4); N5–C25 1.420(4); N(6)–C32 1.443(4); C1–Pd1–N3 84.04(11); C17–Pd1–N(6) 84.68(11); N1–C1–N2 117.6(3); C1–N1–C2 126.4(3); N4–C17–N5 116.3(3).

Complexes **4**, **7**, **13**, **16–18**, and **24** exhibit a slightly distorted square planar geometry around the metal centers. The Pd–C<sub>carbene</sub> distances are typical for the single Pd–C bond and are comparable to those reported for the relevant palladium aminocarbene complex *cis*-[PdCl<sub>2</sub>{C(N(H)N=CPh<sub>2</sub>)=N(H)Xyl}(CNXyl)] (1.924(3) Å)<sup>11</sup> and *cis*-[PdCl<sub>2</sub>{C(Ind)=N(H)Cy}(CNCy)] (1.976(3) Å).<sup>25</sup> In all studied complexes, the carbene moieties are roughly planar and the angles around the carbene carbon atoms are near 120°. All the C–N bonds of the carbene fragments have similar length and lies between single CN bond distance (1.469(10) Å in amines<sup>35</sup>) and double CN bond distance (1.279(8) Å in imines<sup>35</sup>). In the isocyanide ligand, the CN bond [C17–N4 1.152(4) for **13** and C15–N4 1.143(8) for **16**, Å] has a normal value for the triple CN bond in Pd–CNR species.<sup>36–38</sup>

## Final remarks

The results from this work may be considered from at least two perspectives. Firstly, we found that the direction of the reaction between the isocyanide-palladium species and benzene-1,*n*-diamines (*n* = 2–4) depends on the position of the amino group in the benzene ring, viz. on different basicity and nucleophilicity of these nucleophiles.<sup>31</sup> Benzene-1,3-diamine **BDA1** reacts with only one isocyanide group of complexes **1** and **2** leading to the typical monodentate Pd-ADC complexes **4** and **5**, respectively. The reaction between benzene-1,4-diamine (**BDA2**) and complexes **1** and **2** includes participation of both amino groups of the nucleophile accomplishing binuclear Pd-ADC **6** and **7**. By contrast, the reaction of benzene-1,2-diamines **BDA3–BDA5** with palladium-isocyanides opens up the route for preparation of a wide range of aminocarbene species of different structure. Thus, a reaction of equimolar amounts of 1,2-diamines **BDA3–BDA5** and *bis*-isocyanide complexes **1–3** (a molar ratio 1:1) affords aminocarbene monocationic complexes **8–16**. Some of them (**13** and **16**) are able to form Chugaev-type *C,C*-chelated *bis*-carbene complexes **17** and **18** at long time exposition of the reaction mixture. The addition of two-fold excess of **BDA3** or **BDA4** (2 equiv) to isocyanide complexes **1–3** leads to *C,N*-chelated *bis*-carbene complexes **19–24**.

Secondly, prepared diaminocarbene complexes represent different types of aminocarbene palladium species and they might be potentially interesting as acyclic diaminocarbene-based catalysts for cross-coupling reactions.<sup>5,6</sup> In this context, palladium complexes with monodentate aminocarbene ligands<sup>10,11,28,29</sup> as well as with *C,C*- and *C,N*-chelated bidentate aminocarbene<sup>14,17,21</sup> have demonstrated an outstanding catalytic efficiency in different organic transformations, including catalysts that outperform the most active phosphine- and NHC-based complexes. At the same time, application of these compounds in other catalyzed organic transformations, e.g., Buchwald–Hartwig amination, or Heck reaction is significantly less studied but worth exploring and works in this direction are underway in our group.

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**Supporting Information.** Crystal data and structure refinement data.



## Experimental

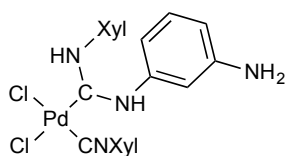
**Materials and Instrumentation.** Solvents, PdCl<sub>2</sub>, benzenediamines, and isocyanides were obtained from commercial sources and used as received, whereas CHCl<sub>3</sub> was purified by the conventional distillation over calcium chloride. Complexes **1–3** were prepared by known procedures.<sup>22</sup> C, H, and N elemental analyses were carried out on a Euro EA 3028HT CHNSO analyzer. Mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source and MeOH, MeCN, or MeOH/DMSO mixture, were used as the solvents. The instrument was operated both at positive and negative ion modes using *m/z* range of 50–3000. The capillary voltage of the ion source was set at –4500 V (ESI<sup>+</sup>) or 3500 V (ESI<sup>–</sup>) and the capillary exit at ±(70–150) V. The nebulizer gas pressure was 0.4 bars and drying gas flow 4.0 L/min. The most intensive peak in the isotopic pattern is reported. Infrared spectra (4000–400 cm<sup>–1</sup>) were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. 1D (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}), DEPT) NMR spectra were acquired on a Bruker Avance 400 spectrometers, while 2D (<sup>1</sup>H,<sup>1</sup>H-COSY, <sup>1</sup>H,<sup>13</sup>C-HMQC/HSQC, and <sup>1</sup>H,<sup>13</sup>C-HMBC) NMR correlation experiments were recorded on Bruker Avance II+ 500 MHz (UltraShield Magnet) spectrometers, at ambient temperature.

**X-ray Structure Determinations.** The crystals of **4**, **7**, **13**, **16–18**, and **24** were immersed in Fomblin® oil (Aldrich), mounted in a Nylon loop, and measured at 100–123 K. The X-ray diffraction data were collected on a Bruker Kappa Apex II, Bruker Kappa Apex II Duo, or Agilent SuperNova diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *Apex2*<sup>39</sup> or *CrysAlisPro*<sup>40</sup> program packages were used for cell refinements and data reductions. The structures were solved by direct methods using the *SHELXS-97*<sup>41</sup> or charge flipping method using *Superflip*<sup>42</sup> programs. A semi-empirical or analytical absorption correction (*SADABS*<sup>43</sup> or *CrysAlisPro*<sup>40</sup>) was applied to all data. Structural refinements were carried out using *SHELXL-97*.<sup>41</sup> Due to slight disorder the carbon C16 in structure **7** was restrained so that its U<sub>ij</sub> components approximate to isotropic

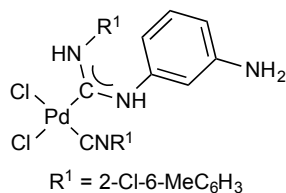
behavior. In **13**, the chlorine and methyl substituents (Cl2 and C8) on one of the aromatic rings were disordered over alternative sides of the ring with occupancy ratio of 0.76/0.24. The C–C and C–Cl distances were restrained to be similar on both sides of the ring. Also, the anisotropic displacement parameter of the alternative C and Cl were set to be equal. The crystals of **16** and **17** were diffracting only weakly. All 1-chloro-3-methylbenzene groups in these structures were disordered in such a way that the Me and Cl groups were flipping over alternative side of the ring. Therefore, a series of geometric and displacement restraints and constraints were applied to these disordered groups. In **18**, the chlorine (Cl3 and Cl6) and the methyl (C8 and C22) substituents on the aromatic rings were again disordered over alternative sides of the ring with occupancy ratios of 0.61/0.39 and 0.77/0.23. The C–Cl and C–C distances were restrained to be similar on both sides of the ring and the anisotropic displacement parameters of the disordered C and Cl atoms were set to be equal. The NH and NH<sub>2</sub> hydrogen atoms were located from the difference Fourier map or positioned geometrically and refined isotropically or constrained to ride on their parent atom, with  $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{parent atom})$ . Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–1.00 and  $U_{\text{iso}} = 1.2\text{--}1.5 U_{\text{eq}}(\text{parent atom})$ . The crystallographic details are summarized in **Table S1**. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCD 1435500–1435506) and can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Synthetic work

**Synthesis of 4 and 5.** Solid **BDA1** (0.1 mmol) was added to the suspension of isocyanide complex (**1** or **2**, 0.1 mmol) in MeCN (5 mL). The reaction mixture was stirred at RT for 3 h and then left overnight. The precipitate was filtered off, washed with Et<sub>2</sub>O (three 1-mL portions) and dried in air at RT.



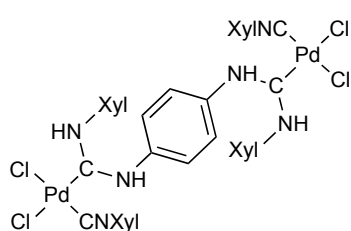
**4.** Yield 76%. Calc. for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 52.62; H, 4.78; N, 10.23. Found: C, 52.60; H, 4.78; N, 10.20. HRESI<sup>+</sup>-MS (70 V, MeOH, *m/z*): calc. for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>CIPd<sup>+</sup> 511.0875, found 511.0881 [M – Cl]<sup>+</sup>, calc. for C<sub>24</sub>H<sub>25</sub>N<sub>4</sub>Pd<sup>+</sup> 475.1109, found 475.1110 [M – 2Cl – H]<sup>+</sup>. HRESI<sup>–</sup>-MS (–70 V, MeOH, *m/z*): calc. for C<sub>24</sub>H<sub>25</sub>N<sub>4</sub>Cl<sub>2</sub>Pd<sup>–</sup> 545.0497, found 545.0509 [M – H]<sup>–</sup>. IR (KBr, selected bands, cm<sup>–1</sup>): ν(N–H) 3322–3268 (m) and 3157 (m), ν(C–H) 2991 (m), ν(C≡N) 2198 (s), ν(N–C<sub>carbene</sub>) 1551 (s), δ(N–H) 1505 (s), δ(C–H Ar) 775 (s). δ<sub>H</sub> (400.130 MHz, DMSO-d<sub>6</sub>): 2.25 (6H, s, CH<sub>3</sub>), 2.31 (6H, s, CH<sub>3</sub>), 5.41 (2H, br, NH<sub>2</sub>), 6.51 (1H, d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, H<sub>Ar</sub>), 6.59 (1H, s, H<sub>Ar</sub>), 7.08 (1H, t, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, H<sub>Ar</sub>), 7.14–7.23 (4H, m, H<sub>Ar</sub>), 7.27 (2H, d, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, H<sub>Ar</sub>), 7.38 (1H, t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, H<sub>Ar</sub>), 9.40 (1H, s, NH), 10.74 (1H, s, NH). δ<sub>C</sub> (100.613 MHz, DMSO-d<sub>6</sub>): 18.3 and 18.4 (CH<sub>3</sub>), 111.3, 112.9 and 113.7 (CH<sub>Ar</sub>), 118.5 (C, C≡N), 125.5 (C<sub>Ar</sub>), 126.6, 128.8, 129.0, 129.4 and 130.8 (CH<sub>Ar</sub>), 134.9, 135.7, 135.8 and 141.5 (C<sub>Ar</sub>), 178.3 (C<sub>carbene</sub>).



**5.** Yield 80%. Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>4</sub>Pd: C, 44.89; H, 3.42; N, 9.52. Found: C, 45.32; H, 3.40; N, 9.48. HRESI<sup>+</sup>-MS (70 V, MeOH, *m/z*): calc. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>3</sub>Pd<sup>+</sup> 550.9783, found 550.9791 [M – Cl]<sup>+</sup>, calc. for C<sub>22</sub>H<sub>19</sub>N<sub>4</sub>Cl<sub>2</sub>Pd<sup>+</sup> 515.0016, found 515.0018 [M – 2Cl – H]<sup>+</sup>. IR (KBr, selected bands, cm<sup>–1</sup>): ν(N–H) 3416–3188 (m) and 3067 (m), ν(C–H) 2924 (m), ν(C–H) 2854 (m), ν(C–H) 2806 (m), ν(C≡N) 2197 (s), ν(N–C<sub>carbene</sub>) 1553 (s), δ(N–H) 1497 (s), δ(C–H Ar) 781 (s). δ<sub>H</sub> (400.130 MHz, DMSO-d<sub>6</sub>): 2.26 (3H, s, CH<sub>3</sub>), 2.34 (3H, s, CH<sub>3</sub>), 6.52–6.58 (2H, m, H<sub>Ar</sub>), 7.22–7.59 (8H, m, H<sub>Ar</sub>), 9.76 (1H, s, NH), 11.08 (1H, s, NH). δ<sub>C</sub> (100.613 MHz, DMSO-d<sub>6</sub>): 18.3 and 18.4 (CH<sub>3</sub>), 111.3, 112.9

and 113.7 (CH<sub>Ar</sub>), 118.5 (C, C≡N), 125.5 (C<sub>Ar</sub>), 126.6, 128.8, 129.0, 129.4 and 130.8 (CH<sub>Ar</sub>), 134.9, 135.7, 135.8 and 141.5 (C<sub>Ar</sub>), 178.3 (C<sub>carbene</sub>).

**Synthesis of 6 and 7.** The mixture containing **BDA2** (0.05 mmol) and isocyanide complex (**1** or **2**, 0.10 mmol) in CHCl<sub>3</sub> (10 mL) was refluxed for 4 h. The yielded precipitate was filtered off, washed with CHCl<sub>3</sub> (two 1-mL portions) and dried in air at RT.



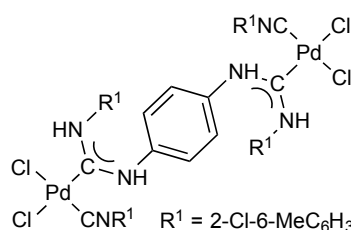
**6.** Yield 74%. Calc. for C<sub>42</sub>H<sub>44</sub>N<sub>6</sub>Cl<sub>4</sub>Pd<sub>2</sub>: C, 51.08; H, 4.49; N, 8.51.

Found: C, 51.01; H, 4.48; N, 8.43. HRESI<sup>+</sup>-MS (70 V, MeOH, *m/z*):

calc. for C<sub>42</sub>H<sub>44</sub>N<sub>6</sub>Cl<sub>3</sub>Pd<sub>2</sub><sup>+</sup> 949.0757, found 949.0764 [M – Cl]<sup>+</sup>, calc.

for C<sub>42</sub>H<sub>44</sub>N<sub>6</sub>Cl<sub>2</sub>Pd<sub>2</sub><sup>2+</sup> 458.0534, found 458.0563 [M – 2Cl]<sup>2+</sup>. IR (KBr,

selected bands, cm<sup>-1</sup>): ν(N–H) 3286–3269 (m), ν(C–H) 2953–2851 (m), ν(C≡N) 2199 (s), ν(N–C<sub>carbene</sub>) 1550 (s), δ(N–H) 1516 (s), δ(C–H Ar) 775 (s). δ<sub>H</sub> (400.130 MHz, DMSO-*d*<sub>6</sub>): 2.28 (6H, s, CH<sub>3</sub>), 2.38 (6H, s, CH<sub>3</sub>), 7.30–7.60 (12H, m, H<sub>Ar</sub>), 7.70–7.90 (4H, m, H<sub>Ar</sub>), 9.99 (1H, s, NH), 11.25 (1H, s, NH). δ<sub>C</sub> (100.613 MHz, DMSO-*d*<sub>6</sub>): 18.6 and 19.0 (8CH<sub>3</sub>), 128.9–136.0 (30C, CH<sub>Ar</sub>), 179.4 (C<sub>carbene</sub>), the isocyanide C signal was not detected.



**7.** Yield 80%. Calc. for C<sub>38</sub>H<sub>32</sub>N<sub>6</sub>Cl<sub>8</sub>Pd<sub>2</sub>: C, 42.69; H, 3.02; N, 7.86.

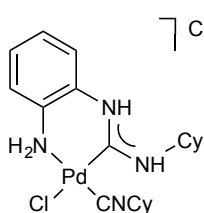
Found: C, 42.59; H, 3.00; N, 7.79. HRESI<sup>+</sup>-MS (70 V, MeOH, *m/z*):

calc. for C<sub>38</sub>H<sub>32</sub>N<sub>6</sub>Cl<sub>7</sub>Pd<sub>2</sub><sup>+</sup> 1028.8572, found 1028.8586 [M – Cl]<sup>+</sup>,

calc. for C<sub>38</sub>H<sub>32</sub>N<sub>6</sub>Cl<sub>6</sub>Pd<sub>2</sub><sup>2+</sup> 498.9427, found 498.9477 [M – 2Cl]<sup>2+</sup>. IR

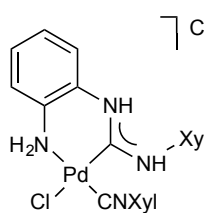
(KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3230–3180 (m), ν(C–H) 2957–2852 (m), ν(C≡N) 2200 (s), ν(N–C<sub>carbene</sub>) 1544 (s), δ(N–H) 1508 (s), δ(C–H Ar) 777 (s). δ<sub>H</sub> (400.130 MHz, DMSO-*d*<sub>6</sub>): 2.28 (6H, s, CH<sub>3</sub>), 2.38 (6H, s, CH<sub>3</sub>), 7.30–7.60 (12H, m, H<sub>Ar</sub>), 7.70–7.90 (4H, m, H<sub>Ar</sub>), 9.99 (1H, s, NH), 11.25 (1H, s, NH); δ<sub>C</sub> (100.613 MHz, DMSO-*d*<sub>6</sub>): 18.8 and 19.3 (4C, CH<sub>3</sub>), 124.1–129.2 (30C, CH<sub>Ar</sub>), 180.4 (C<sub>carbene</sub>), the isocyanide C signal was not detected.

**Synthesis of 8–16.** The solid benzenediamines (**BDA3–BDA5**; 0.1 mmol) were added to the solution or suspension of any one of **1–3** (0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), and the reaction mixture left at RT overnight. The yielded precipitate was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and dried in air at RT (portion 1). The initial solution and the filtrate were combined, dried in vacuo at RT, washed with cooled mixture of Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> 9:1 (1 mL), then Et<sub>2</sub>O (two 1-mL portions), and dried in air at RT (portion 2).

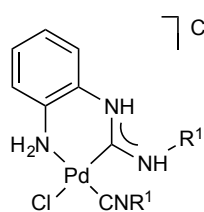


**8.** Yield 69%. Calc. for C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 47.68; H, 6.00; N, 11.12. Found: C, 47.67; H, 5.96; N, 11.13. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>20</sub>H<sub>30</sub>N<sub>4</sub>ClPd<sup>+</sup> 467.1188, found *m/z* 467.1191 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3429 (m), ν(C–H) 2932–2852 (m), ν(C≡N) 2233 (s), ν(N–C<sub>carbene</sub>) 1570 (s),

δ(N–H) 1500 (s), δ(C–H Ar) 757 (s). δ<sub>H</sub> (400.130 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 0.95–2.20 (20H, m, CH<sub>2</sub>), 3.65–3.80 (1H, m, CH from Cy), 3.85–4.00 (1H, m, CH from Cy), 6.94 (1H, d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, H<sub>Ar</sub>), 7.05–7.12 (2H, m, H<sub>Ar</sub>), 7.23 (1H, d, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, H<sub>Ar</sub>), 9.60 (1H, d, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, C<sub>carbene</sub>–NH–Cy), 11.07 (1H, s, NH). δ<sub>C</sub> (100.613 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 22.7, 24.5, 24.7, 24.9, 31.9, and 33.8 (CH<sub>2</sub> from Cy), 55.8 and 59.2 (CH from Cy), 121.3, 121.9, 125.0, and 126.9 (CH<sub>Ar</sub>), 128.2 and 135.9 (C<sub>Ar</sub>), 178.9 (C<sub>carbene</sub>), signal from isocyanide C was not detected.

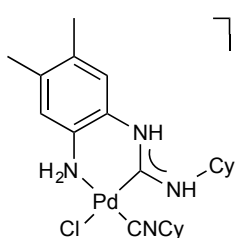


**9.** Yield 78%. Calc. for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 52.62; H, 4.78; N, 10.23. Found: C, 52.64; H, 4.80; N, 10.23. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>24</sub>H<sub>26</sub>N<sub>4</sub>ClPd<sup>+</sup> 511.0875, found *m/z* 511.0883 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3447 (m), ν(C–H) 2950 (m), ν(C≡N) 2207 (s), ν(N–C<sub>carbene</sub>) 1552 (s), δ(N–H) 1503 (s), δ(C–H Ar) 776 (m). δ<sub>H</sub> (400.130 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 2.14 (6H, s, CH<sub>3</sub>), 2.57 (6H, s, CH<sub>3</sub>), 6.79–7.33 (10H, m, H<sub>Ar</sub>), 11.06 (1H, s, NH), 12.35 (1H, s, NH). δ<sub>C</sub> (100.613 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 18.3 and 19.9 (CH<sub>3</sub>), 121.2, 122.3 and 125.5 (CH<sub>Ar</sub>), 127.2 (C<sub>Ar</sub>), 127.3, 127.8, 128.1 and 128.3 (CH<sub>Ar</sub>), 129.3 (C<sub>Ar</sub>), 130.1 (CH<sub>Ar</sub>), 135.2, 135.6 and 137.8 (C<sub>Ar</sub>), 183.7 (C<sub>carbene</sub>), signal from isocyanide C was not detected.

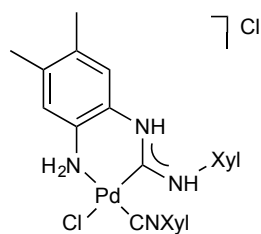


R<sup>1</sup> = 2-Cl-6-MeC<sub>6</sub>H<sub>3</sub>

Cl **10.** Yield 72%. Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>4</sub>Pd: C, 48.89; H, 3.42; N, 9.52. Found: C, 48.93; H, 3.44; N, 9.53. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>Cl<sub>3</sub>Pd<sup>+</sup> 550.9783, found *m/z* 550.9788 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3446–3130 (m), ν(C–H) 2962 (m), ν(C≡N) 2210 (s), ν(N–C<sub>carbene</sub>) 1556 (s), δ(N–H) 1503 (s), δ(C–H Ar) 784 (m). δ<sub>H</sub> (400.130 MHz, CD<sub>3</sub>OD): 2.50 (3H, s, CH<sub>3</sub>), 2.59 (3H, s, CH<sub>3</sub>), 7.14–7.63 (10H, m, H<sub>Ar</sub>). δ<sub>C</sub> (100.613 MHz, CD<sub>3</sub>OD): 17.4 and 17.8 (CH<sub>3</sub>), 121.9, 122.4, 126.6, 126.7, 127.5 and 128.0 (CH<sub>Ar</sub>), 129.2 (C<sub>Ar</sub>), 129.3 (CH<sub>Ar</sub>), 129.8 (C<sub>Ar</sub>), 130.0 and 130.4 (CH<sub>Ar</sub>), 130.9 and 131.4 (C<sub>Ar</sub>), 131.8 (CH<sub>Ar</sub>), 132.6, 135.3, 138.0 and 139.2 (C<sub>Ar</sub>), 177.0 (C<sub>carbene</sub>), signal from isocyanide C was not detected.

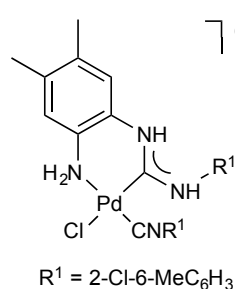


Cl **11.** Yield 77%. Calc. for C<sub>22</sub>H<sub>34</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 49.68; H, 6.44; N, 10.53. Found: C, 49.78; H, 6.50; N, 10.48. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>22</sub>H<sub>34</sub>N<sub>4</sub>ClPd<sup>+</sup> 495.1501, found *m/z* 495.1503 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3430 (m), ν(C–H) 2935–2850 (m), ν(C≡N) 2235 (s), ν(N–C<sub>carbene</sub>) 1570 (s), δ(N–H) 1500 (s), δ(C–H Ar) 755 (s). δ<sub>H</sub> (400.130 MHz, CDCl<sub>3</sub>): 0.76–2.00 (20H, m, CH<sub>2</sub>), 2.09 (3H, s, CH<sub>3</sub>), 2.18 (3H, s, CH<sub>3</sub>), 3.55–3.70 (1H, m, CH), 3.77–3.87 (1H, m, CH), 6.72 (1H, s, H<sub>Ar</sub>), 6.92 (1H, s, H<sub>Ar</sub>), 9.40 (1H, d, <sup>3</sup>J<sub>H,H</sub> = 8.9 Hz, C<sub>carbene</sub>–NH–Cy), 10.90 (1H, s, NH). δ<sub>C</sub> (100.613 MHz, CDCl<sub>3</sub>): 19.1, 22.7, 24.5, 24.7, 24.9 and 31.9 (CH<sub>2</sub>), 55.6 and 59.1 (CH), 122.4 and 122.9 (CH<sub>Ar</sub>), 125.2, 133.4, 133.7 and 135.2 (C<sub>Ar</sub>), 178.5 (C<sub>carbene</sub>), signal from isocyanide C was not detected.

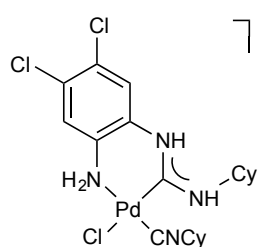


Cl **12.** Yield 73%. Calc. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 54.23; H, 5.25; N, 9.73. Found: C, 54.17; H, 5.19; N, 9.68. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>ClPd 539.1188, found *m/z* 539.1194 [M – Cl]<sup>+</sup>. HRESI<sup>-</sup>-MS (–70 V, MeOH, *m/z*): calc. for C<sub>26</sub>H<sub>28</sub>N<sub>4</sub>ClPd<sup>+</sup> 537.1032, found 539.1044 [M – Cl – 2H]<sup>-</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3446 (m), ν(C–H) 2950 (m), ν(C≡N) 2203 (s), ν(N–C<sub>carbene</sub>) 1555 (s), δ(N–H) 1513 (s), δ(C–H Ar) 781 (m). δ<sub>H</sub> (400.130 MHz, CDCl<sub>3</sub>): 1.99 (3H, s, CH<sub>3</sub>), 2.09 (6H, s, CH<sub>3</sub>), 2.15 (3H, s, CH<sub>3</sub>), 2.54 (6H, s, CH<sub>3</sub>), 6.74–6.82 (3H, m, H<sub>Ar</sub>), 6.84 (1H, s,

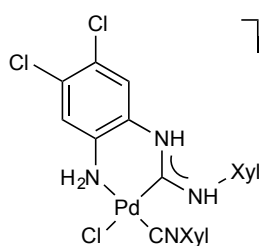
H<sub>Ar</sub>), 6.98–7.00 (3H, m, H<sub>Ar</sub>), 7.15–7.19 (1H, m, H<sub>Ar</sub>), 10.70 (1H, s, NH), 12.14 (1H, s, NH).  $\delta_C$  (100.613 MHz, CDCl<sub>3</sub>): 18.5 (2C, CH<sub>3</sub>), 18.9 and 19.0 (CH<sub>3</sub>), 20.1 (2C, CH<sub>3</sub>), 122.3 and 123.4 (CH<sub>Ar</sub>), 124.3 (C<sub>Ar</sub>), 127.8 and 127.9 (CH<sub>Ar</sub>), 128.2 (C<sub>Ar</sub>), 128.3 and 130.1 (CH<sub>Ar</sub>), 133.0, 134.3, 135.2, 135.7 and 135.8 (C<sub>Ar</sub>), 137.8 (CH<sub>Ar</sub>), 183.0 (C<sub>carbene</sub>), signal from isocyanide C was not detected.



**13.** Yield 82%. Calc. for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Cl<sub>4</sub>Pd: C, 46.74; H, 3.92; N, 9.08. Found: C, 46.71; H, 3.98; N, 9.03. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Cl<sub>3</sub>Pd<sup>+</sup> 579.0096, found *m/z* 579.0102 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>):  $\nu$ (N–H) 3440 (m),  $\nu$ (C–H) 2960 (m),  $\nu$ (C≡N) 2210 (s),  $\nu$ (N–C<sub>carbene</sub>) 1556 (s),  $\delta$ (N–H) 1500 (s),  $\delta$ (C–H Ar) 785 (m).  $\delta_H$  (400.130 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 2.13 (3H, s, CH<sub>3</sub>), 2.17 (3H, s, CH<sub>3</sub>), 2.25 (3H, s, CH<sub>3</sub>), 2.29 (3H, s, CH<sub>3</sub>), 6.82–6.90 (3H, m, H<sub>Ar</sub>), 7.08 (1H, s, H<sub>Ar</sub>), 7.11–7.37 (4H, m, H<sub>Ar</sub>), 11.25 (1H, s, NH), 12.54 (1H, s, NH).  $\delta_C$  (100.613 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 18.7, 18.8, 18.9 and 19.8 (CH<sub>3</sub>), 122.4–138.0 (18C, C<sub>Ar</sub>), 182.9 (C<sub>carbene</sub>), signal from isocyanide C was not detected.

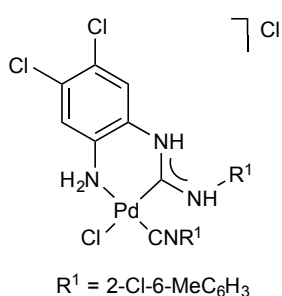


**14.** Yield 52%. Calc. for C<sub>20</sub>H<sub>28</sub>N<sub>4</sub>Cl<sub>4</sub>Pd: C, 41.94; H, 4.93; N, 9.78. Found: C, 42.07; H, 4.96; N, 9.73. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>20</sub>H<sub>28</sub>N<sub>4</sub>Cl<sub>3</sub>Pd<sup>+</sup> 535.0409, found *m/z*: 535.0415 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>):  $\nu$ (N–H) 3483–3175 (m),  $\nu$ (C–H) 2935–2857 (m),  $\nu$ (C≡N) 2240 (s),  $\nu$ (N–C<sub>carbene</sub>) 1566 (s),  $\delta$ (N–H) 1586 (s).  $\delta_H$  (400.130 MHz, CD<sub>3</sub>OD): 1.22–2.18 (20H, m, CH<sub>2</sub>), 4.00–4.10 (1H, m, CH), 4.10–4.20 (1H, m, CH), 7.61 (1H, s, H<sub>Ar</sub>), 7.62 (1H, s, H<sub>Ar</sub>).  $\delta_C$  (100.613 MHz, CD<sub>3</sub>OD): 22.2, 24.3, 24.5, 24.4, 31.3 and 31.9 (CH<sub>2</sub>), 54.7 and 55.4 (CH), 123.0 and 123.1 (CH<sub>Ar</sub>), 128.4, 129.3, 129.4 and 135.6 (C<sub>Ar</sub>), 173.7 (C<sub>carbene</sub>), signal from isocyanide C was not detected.



**15.** Yield 60%. Calc. for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Cl<sub>4</sub>Pd: C, 46.74; H, 3.92; N, 9.08. Found: C, 46.80; H, 3.97; N, 9.10. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>Cl<sub>3</sub>Pd<sup>+</sup> 579.0096, found *m/z* 579.0098 [M – Cl]<sup>+</sup>. IR (KBr,

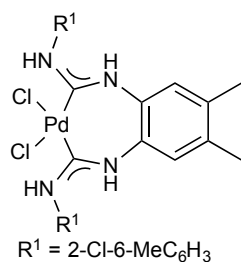
selected bands,  $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3286–3012 (m),  $\nu(\text{C-H})$  2831–2756 (m),  $\nu(\text{C}\equiv\text{N})$  2203 (s),  $\nu(\text{N-C}_{\text{carbene}})$  1553 (s),  $\delta(\text{N-H})$  1476 (s),  $\delta(\text{C-H Ar})$  801 (s).  $\delta_H$  (400.130 MHz,  $\text{CD}_3\text{OD}$ ): 2.41 (6H, s,  $\text{CH}_3$ ), 2.52 (6H, s,  $\text{CH}_3$ ), 7.24–7.40 (6H, m,  $\text{H}_{\text{Ar}}$ ), 7.42 (1H, s,  $\text{H}_{\text{Ar}}$ ), 7.73 (1H, s,  $\text{H}_{\text{Ar}}$ ).  $\delta_C$  (100.613 MHz,  $\text{CD}_3\text{OD}$ ): 17.2 and 17.5 ( $\text{CH}_3$ ), 123.4, 124.0, 128.1 and 129.0 ( $\text{CH}_{\text{Ar}}$ ), 129.1 ( $\text{C}_{\text{Ar}}$ ), 129.5 ( $\text{CH}_{\text{Ar}}$ ), 133.8, 134.9, 135.2 and 136.3 ( $\text{C}_{\text{Ar}}$ ), 177.0 ( $\text{C}_{\text{carbene}}$ ), signal from isocyanide C was not detected.



**16.** Yield 66%. Calc. for  $\text{C}_{22}\text{H}_{18}\text{N}_4\text{Cl}_6\text{Pd}$ : C, 40.19; H, 2.76; N, 8.52. Found: C, 40.27; H, 2.86; N, 8.44. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for  $\text{C}_{22}\text{H}_{18}\text{N}_4\text{Cl}_5\text{Pd}^+$  618.9003, found  $m/z$  618.9012  $[\text{M} - \text{Cl}]^+$ . IR (KBr, selected bands,  $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3443–3111 (m),  $\nu(\text{C-H})$  2924 (m),  $\nu(\text{C}\equiv\text{N})$  2208 (s),  $\nu(\text{N-C}_{\text{carbene}})$  1550 (s),  $\delta(\text{N-H})$  1487 (s),  $\delta(\text{C-H Ar})$  780 (s).  $\delta_H$

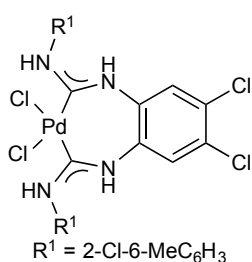
(400.130 MHz,  $\text{CD}_3\text{OD}$ ): 2.47 (6H, s,  $\text{CH}_3$ ), 2.57 (6H, s,  $\text{CH}_3$ ), 7.35–7.54 (7H, m,  $\text{H}_{\text{Ar}}$ ), 7.72 (1H, s,  $\text{H}_{\text{Ar}}$ ).  $\delta_C$  (100.613 MHz,  $\text{CD}_3\text{OD}$ ): 17.4 and 17.8 ( $\text{CH}_3$ ), 123.4, 123.8, 127.4, 128.0 and 129.2 ( $\text{CH}_{\text{Ar}}$ ), 129.3 and 129.9 ( $\text{C}_{\text{Ar}}$ ), 130.0 and 130.6 ( $\text{CH}_{\text{Ar}}$ ), 130.9, 131.2 and 131.6 ( $\text{C}_{\text{Ar}}$ ), 131.8 ( $\text{CH}_{\text{Ar}}$ ), 132.2 ( $\text{C}_{\text{Ar}}$ ), 137.9 and 139.4 (CH, Ar), 177.6 ( $\text{C}_{\text{carbene}}$ ), signal from isocyanide C was not detected.

**Synthesis of 17 and 18.** The solutions of **13** and **16** (0.05 mmol) in MeCN (10 mL) were evaporated slowly at RT for 2 months. A few crystals of formed **17** and **18** were mechanically separated and studied by HRESI-MS and X-ray crystallography.



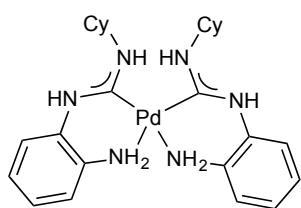
**17.** HRESI<sup>+</sup>-MS (70 V, MeOH,  $m/z$ ): calc. for  $\text{C}_{24}\text{H}_{24}\text{N}_4\text{Cl}_3\text{Pd}^+$  579.0096, found 579.0081  $[\text{M} - \text{Cl}]^+$ . IR (KBr, selected bands,  $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3217–3085 (m),  $\nu(\text{C-H})$  2960 (m),  $\nu(\text{N-C}_{\text{carbene}})$  1560 (s),  $\delta(\text{N-H})$  1505 (s),  $\delta(\text{C-H Ar})$  785 (s).



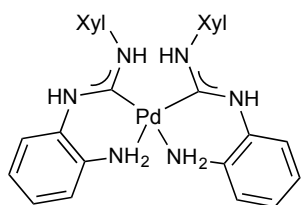


**18.** HRESI<sup>+</sup>-MS (70 V, MeOH, *m/z*): calc. for C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>Cl<sub>5</sub>Pd<sup>+</sup> 618.9003, found 618.8989 [M – Cl]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3243–3090 (m), ν(C–H) 2940 (m), ν(N–C<sub>carbene</sub>) 1560 (s), δ(N–H) 1500 (s), δ(C–H Ar) 780 (s).

**Synthesis of 19–24.** A solution of diamine (**BDA3** or **BDA4**, 0.22 mmol) in MeCN (1 mL) was slowly added at RT to a solution or suspension of any one of **1–3** (0.10 mmol) in MeCN (2 mL). The color of the reaction mixture turned immediately from light yellow to bright yellow, which gradually turned back to the light yellow. For all complexes except **22** the reaction mixture was stirred for 1h at RT until a crystalline precipitate formed; complex **22** was obtained via heating up to 70 °C for 2 h and cooling to RT. The formed precipitates were filtered off, washed with MeCN (1 mL) and Et<sub>2</sub>O (two 1-mL portions) and dried in air at RT.

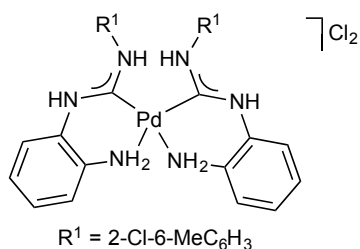


**19.** Yield 80%. Calc. for C<sub>26</sub>H<sub>38</sub>N<sub>6</sub>Cl<sub>2</sub>Pd: C, 51.03; H, 6.26; N, 11.59. Found: C, 50.98; H, 6.25; N, 13.73. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for C<sub>26</sub>H<sub>38</sub>N<sub>6</sub>ClPd<sup>+</sup> 575.1876, found *m/z* 575.1883 [M – Cl]<sup>+</sup>, calc. for C<sub>26</sub>H<sub>37</sub>N<sub>6</sub>Pd<sup>+</sup> 539.2109, found *m/z* 539.2113 [M – 2Cl – H]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3429 (m), ν(C–H) 2932–2855 (m), ν(N–C<sub>carbene</sub>) 1562 (s), δ(N–H) 1500 (s), δ(C–H Ar) 754 (s). δ<sub>H</sub> (400.130 MHz, CD<sub>3</sub>OD): 1.10–2.10 (20H, m, CH<sub>2</sub>), 3.85–4.05 (2H, m, NH-CH), 7.10–7.35 (5H, m, Ar), 7.35–7.45 (1H, m, H<sub>Ar</sub>), 7.45–7.56 (2H, m, H<sub>Ar</sub>). δ<sub>C</sub> (100.613 MHz, CD<sub>3</sub>OD): 24.5, 24.9 and 31.8 (CH<sub>2</sub>), 52.6 (CH-NH), 121.4, 122.3, 125.2 and 125.7 (CH<sub>Ar</sub>), 130.8 and 135.8 (C<sub>Ar</sub>), 183.5 (C<sub>carbene</sub>).



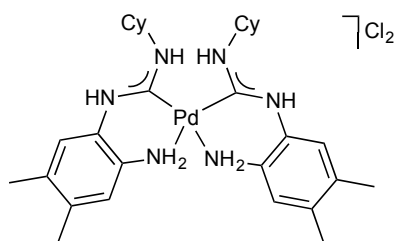
**20.** Yield 91%. Calc. for C<sub>30</sub>H<sub>34</sub>N<sub>6</sub>Cl<sub>2</sub>Pd: C, 54.93; H, 5.22; N, 12.81. Found: C, 54.94; H, 5.23; N, 12.83. HRESI<sup>+</sup>-S (70 V, MeOH): calc. for C<sub>30</sub>H<sub>34</sub>ClN<sub>6</sub>Pd<sup>+</sup> 619.1563, found *m/z* 619.1567 [M – Cl]<sup>+</sup>, calc. for C<sub>30</sub>H<sub>33</sub>N<sub>6</sub>Pd<sup>+</sup> 583.1796, found *m/z* 583.1799 [M – 2Cl – H]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): ν(N–H) 3410 (m), ν(C–H) 2980 (m), ν(N–C<sub>carbene</sub>)

1545 (s),  $\delta(\text{N-H})$  1500 (s),  $\delta(\text{C-H Ar})$  780 (m).  $\delta_H$  (400.130 MHz,  $\text{CD}_3\text{OD}$ ): 2.38 (12H, s,  $\text{CH}_3$ ), 7.20–7.35 (12H, m,  $\text{H}_{\text{Ar}}$ ), 7.55–7.65 (2H, m,  $\text{H}_{\text{Ar}}$ ).  $\delta_C$  (100.613 MHz,  $\text{CD}_3\text{OD}$ ): 18.0 (4C,  $\text{CH}_3$ ), 122.3, 123.8, 126.3, 126.4, 129.3 and 129.5 ( $\text{CH}_{\text{Ar}}$ ), 131.8, 134.1, 135.8 and 135.9 ( $\text{C}_{\text{Ar}}$ ), 186.3 ( $\text{C}_{\text{carbene}}$ ).



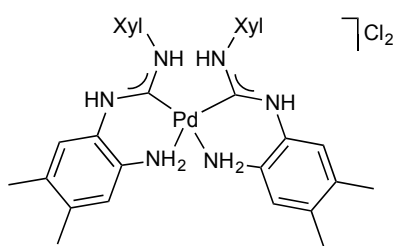
**21.** Yield 87%. Calc. for  $\text{C}_{28}\text{H}_{28}\text{N}_6\text{Cl}_4\text{Pd}$ : C, 48.26; H, 4.05; N, 12.06. Found: C, 48.27; H, 4.07; N, 12.08. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for  $\text{C}_{28}\text{H}_{28}\text{N}_6\text{Cl}_3\text{Pd}^+$  659.0470, found  $m/z$  659.0473  $[\text{M} - \text{Cl}]^+$ , calc. for  $\text{C}_{28}\text{H}_{27}\text{N}_6\text{Cl}_2\text{Pd}^+$  623.0704, found  $m/z$  623.0709

$[\text{M} - 2\text{Cl} - \text{H}]^+$ . IR (KBr, selected bands,  $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3408 (m),  $\nu(\text{C-H})$  2979 (m),  $\nu(\text{N-C}_{\text{carbene}})$  1546 (s),  $\delta(\text{N-H})$  1502 (s),  $\delta(\text{C-H Ar})$  778 (m).  $\delta_H$  (400.130 MHz,  $\text{CD}_3\text{OD}$ ): 2.44 (3H, s,  $\text{CH}_3$ ), 2.46 (3H, s,  $\text{CH}_3$ ), 7.22–7.27 (6H, m,  $\text{H}_{\text{Ar}}$ ), 7.36–7.41 (4H, m,  $\text{H}_{\text{Ar}}$ ), 7.44–7.50 (2H, m,  $\text{H}_{\text{Ar}}$ ), 7.60–7.65 (2H, m,  $\text{H}_{\text{Ar}}$ ).  $\delta_C$  (100.613 MHz,  $\text{CD}_3\text{OD}$ ): 17.8 (2C,  $\text{CH}_3$ ), 122.0, 123.3, 126.0, 126.2, 128.0, 129.9 and 130.2 ( $\text{CH}_{\text{Ar}}$ ), 131.2, 131.8, 131.9, 132.1, 132.2, 135.3, 135.4, 138.6, and 138.7 ( $\text{C}_{\text{Ar}}$ ), 186.7 ( $\text{C}_{\text{carbene}}$ ).

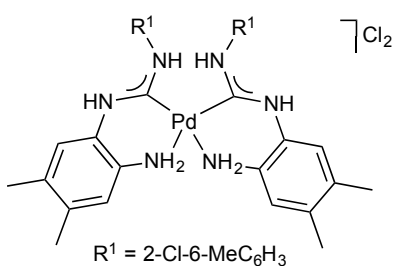


**22.** Yield 85%. Calc. for  $\text{C}_{30}\text{H}_{46}\text{N}_6\text{Cl}_2\text{Pd}$ : C, 53.94; H, 6.94; N, 12.58. Found: C, 53.97; H, 6.98; N, 12.56. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for  $\text{C}_{30}\text{H}_{46}\text{N}_6\text{ClPd}^+$  631.2502, found 631.2507  $[\text{M} - \text{Cl}]^+$ , calc. for  $\text{C}_{30}\text{H}_{45}\text{N}_6\text{Pd}^+$  595.2735, found  $m/z$  595.2742  $[\text{M} - 2\text{Cl} - \text{H}]^+$ . HRESI<sup>-</sup>-MS (–70 V, MeOH,  $m/z$ ): calc. for  $\text{C}_{30}\text{H}_{45}\text{N}_6\text{Cl}_2\text{Pd}^-$  665.2123, found  $m/z$  665.2131  $[\text{M} - \text{H}]^-$ , calc. for  $\text{C}_{30}\text{H}_{44}\text{N}_6\text{ClPd}^-$  629.2356, found  $m/z$  629.2362  $[\text{M} - \text{Cl} - 2\text{H}]^-$ . IR (KBr, selected

bands,  $\text{cm}^{-1}$ ):  $\nu(\text{N-H})$  3430 (m),  $\nu(\text{C-H})$  2935–2850 (m),  $\nu(\text{N-C}_{\text{carbene}})$  1560 (s),  $\delta(\text{N-H})$  1500 (s),  $\delta(\text{C-H Ar})$  753 (s).  $\delta_H$  (400.130 MHz,  $\text{CD}_3\text{OD}$ ): 2.48–3.64 (20H, m,  $\text{CH}_2$ ), 2.23 and 2.25 (16H, s,  $\text{CH}_3$ ), 3.19–3.24 and 3.87–3.93 (2H, m, CH), 6.92, 6.97, 7.12, 7.23, 7.28 and 7.91 (4H, s,  $\text{H}_{\text{Ar}}$ ).  $\delta_C$  (100.613 MHz,  $\text{CD}_3\text{OD}$ ): 17.71, 17.77, 17.81, 17.88, 24.6–25.0, 31.7, 31.9, 32.1, 31.8, 34.5, 52.5, 53.5, 58.5, 59.2, 122.3, 122.4, 122.5, 122.6, 122.9, 123.0, 123.1, 128.1, 128.5, 128.8, 132.8, 133.0, 133.2, 133.3, 133.7, 134.0, 134.2, 134.4, 134.5, 134.6, 134.7, 183.1 and 189.9 ( $\text{C}_{\text{carbene}}$ ).



**23.** Yield 93%. Calc. for  $C_{34}H_{42}N_6Cl_2Pd$ : C, 57.35; H, 5.95; N, 11.80. Found: C, 57.37; H, 5.48; N, 11.83. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for  $C_{34}H_{42}N_6ClPd^+$  675.2189, found  $m/z$  675.2195  $[M - Cl]^+$ , calc. for  $C_{34}H_{41}N_6Pd^+$  639.2422, found  $m/z$  639.2419  $[M - 2Cl - H]^+$ . HRESI<sup>-</sup>-MS (-70 V, MeOH,  $m/z$ ): calc. for  $C_{34}H_{40}N_6ClPd^-$  673.2043, found  $m/z$  673.2047  $[M - Cl - 2H]^-$ . IR (KBr, selected bands,  $cm^{-1}$ ):  $\nu(N-H)$  3423 (m),  $\nu(C-H)$  2958 (m),  $\nu(N-C_{\text{carbene}})$  1546 (s),  $\delta(N-H)$  1511 (s),  $\delta(C-H \text{ Ar})$  780 (s).  $\delta_H$  (400.130 MHz,  $CD_3OD$ ): 2.21 (6H, s,  $CH_3$ ), 2.25 (6H, s,  $CH_3$ ), 2.37 (12H, s,  $CH_3$ ), 6.97 (2H, s,  $H_{Ar}$ ), 7.20–7.30 (6H, m,  $H_{Ar}$ ), 7.39 (2H, s,  $H_{Ar}$ ).  $\delta_C$  (100.613 MHz,  $CD_3OD$ ): 19.0–19.2 (8C,  $CH_3$ ), 124.1 and 125.5 ( $CH_{Ar}$ ), 129.9 ( $C_{Ar}$ ), 130.2 and 130.3 ( $CH_{Ar}$ ), 134.2, 135.1, 135.7, 136.0 and 136.9 ( $C_{Ar}$ ), 186.9 ( $C_{\text{carbene}}$ ).



**24.** Yield 88%. Calc. for  $C_{32}H_{36}N_6Cl_4Pd$ : C, 51.05; H, 4.82; N, 11.16. Found: C, 51.07; H, 4.80; N, 11.13. HRESI<sup>+</sup>-MS (70 V, MeOH): calc. for  $C_{32}H_{35}N_6Cl_2Pd^+$  679.1330, found  $m/z$  679.1334  $[M - 2Cl - H]^+$ . HRESI<sup>-</sup>-MS (-70 V, MeOH,  $m/z$ ): calc. for  $C_{32}H_{34}N_6Cl_3Pd^-$  713.0951, found 713.0948  $[M - Cl - 2H]^-$ . IR (KBr, selected bands,  $cm^{-1}$ ):  $\nu(N-H)$  3424 (m),  $\nu(C-H)$  2973 (m),  $\nu(N-C_{\text{carbene}})$  1546 (s),  $\delta(N-H)$  1515 (s),  $\delta(C-H \text{ Ar})$  779 (s).  $\delta_H$  (400.130 MHz,  $CD_3OD$ ): 2.22 (6H, s,  $CH_3$ ), 2.26 (6H, s,  $CH_3$ ), 2.42 (3H, s,  $CH_3$ ), 2.43 (3H, s,  $CH_3$ ), 6.99 (2H, s,  $H_{Ar}$ ), 7.36–7.39 (6H, m,  $H_{Ar}$ ), 7.43–7.46 (2H, m,  $H_{Ar}$ ).  $\delta_C$  (100.613 MHz,  $CD_3OD$ ): 19.1–19.2 (6C,  $CH_3$ ), 124.2, 125.4 and 129.3 ( $CH_{Ar}$ ), 129.8 ( $C_{Ar}$ ), 131.3 and 131.5 ( $CH_{Ar}$ ), 133.2, 133.3, 133.5, 133.7, 134.2, 135.8, 136.2, and 140.0 ( $C_{Ar}$ ), 187.6 ( $C_{\text{carbene}}$ ).

**Synthesis of 19–24 from 8–13.** A solution of the corresponding diamine (0.12 mmol) in MeCN (1 mL) was slowly added to a solution or suspension of any one of monocarbene complex **8–13** (0.10 mmol) in MeCN (2 mL). The reaction mixture was stirred for 1 h at RT. The formed colorless solid was filtered off and washed with MeCN (1 mL) and Et<sub>2</sub>O (two 1-mL portions). Yields: **19** (87%), **20** (93%), **21** (85%), **22** (82%), **23** (87%), and **24** (92%).

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## Graphical abstract

