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# Influence of steric effect on the structural aspects of *N*,*N*′,*N*″-triarylguanidine derived six-membered [*C*,*N*] palladacycles

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# ABSTRACT

Guanidine derived six-membered [*C*,*N*] palladacycles of the types  $[(C,N)Pd(\mu-OC(O)R)]_2$  (**1a**-d),  $[(C,N)Pd(\mu-Br)]_2$  (**2a,b**), *cis*-[(C,N)PdBr(L)] (**3a**-d, **4**, and **5**), and ring contracted guanidine derived fivemembered [C,N] palladacycle, [(C,N)PdBr(C)] (**3a**-d, **4**, and **5**), and ring contracted guanidine derived fivemembered [C,N] palladacycle, [(C,N)PdBr(C)] (**3a**-d, **4**, and **5**), and ring contracted guanidine derived fivemembered [C,N] palladacycle, [(C,N)PdBr(C)] (**5**) were prepared in high yield following the established methods with a view aimed at understanding the influence of the substituents on the aryl rings of the guanidine upon the solid state structure and solution behaviour of palladacycles. Palladacycles were characterised by microanalytical, IR, NMR and mass spectral data. The molecular structures of **1a**, **1c**, **2a**, **2b**, **3a**, **3c**, **3d**, and **4**-**6** were determined by single crystal X-ray diffraction data. Palladacycles **1a** and **1c** were shown to exist as a dimer in *transoid* in-in conformation in the solid state but as a mixture of a dimer in major proportion and a monomer ( $\kappa^2$ -0,0'-OAc) in solution as deduced from <sup>1</sup>H NMR data. Palladacycles **2a** and **2b** were shown to exist as a dimer in *transoid* conformation in the solid state but the former was shown to exist as a mixture of a dimer and presumably a trimer in solution as revealed by a variable temperature <sup>1</sup>H NMR data in conjunction with ESI-MS data. The *cis* configuration around the palladium atom in **3a**, **3c**, and **3d** was ascribed to steric influence of the aryl moiety of =NAr unit and that in **4-6** was ascribed to antisymbiosis. The solution behaviour of **3d** was studied by a variable concentration (VC) <sup>1</sup>H NMR data.

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# 1. Introduction

The imine derived six-membered [C,N] palladacycles are one of the interesting classes of palladacycles due their relevance as precatalysts in C–C and C–heteroatom bond forming reactions [1–4], their intriguing structural and reactivity pattern including regioselective aspects of C–H activation process [5–11], and as scaffolds that exhibit interesting photophysical properties [12,13]. Further, the six-membered "[C,N]Pd" skeleton is often encountered as a reactive intermediate in palladium mediated organic transformations [14,15].

*Sym N*,*N*′′,*N*′′-trisubstituted guanidines, RN==C(NHR)<sub>2</sub> (R = alkyl, and aryl) are one of the interesting classes of nitrogen donor ligands as they have the ability to coordinate to the metal ions in their neutral form ( $\kappa^1 N$ ), chelating monoanionic ( $\kappa^2 N$ ,*N*′), bridging monoanionic ( $\mu_2$ - $\kappa^1 N$ ; $\kappa^1 N$ ′), and chelating dianionic forms ( $\kappa^2 N$ ,*N*′) as illustrated in Chart 1 [16,17]. *Sym N*,*N*′,*N*″-triarylguanidines, ArN=C(NHAr)<sub>2</sub> are more basic than the corresponding arylimines due to the ability of the former to form the

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guanidinium salt [(ArNH)<sub>3</sub>C]<sup>+</sup>X<sup>-</sup> upon protonation under facile condition. This feature of *N*,*N*',*N*''-triarylguanidines in conjunction with the ready tunability of the aryl moieties were anticipated to facilitate cyclopalladation reaction upon treatment with palladium(II) carboxylates. We have recently reported the synthesis, reactivity studies, structural aspects, and solution dynamics of  $(ArNH)_2C = NAr (Ar = 2-(MeO)C_6H_4; LH_2^{2-anisyl})$  derived six-membered and ring contracted five-membered [C,N] palladacycles [18]. In these palladacycles, LH<sub>2</sub><sup>2-anisyl</sup> was shown to act as monoanionic [*C*,*N*] donor ligand ( $\kappa^2 C$ ,*N*) to the palladium (Chart 1). We want to address how the sterically more hindered aryl moieties in  $(ArNH)_2C=NAr$  (Ar = 2-MeC<sub>6</sub>H<sub>4</sub> (LH<sub>2</sub><sup>2-tolyl</sup>) and 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (LH<sub>2</sub><sup>2,4-xylyl</sup>)) than those present in LH<sub>2</sub><sup>2-anisyl</sup> and their conformational difference (anti-anti  $\alpha\beta\alpha$  versus syn-anti  $\alpha\beta\beta$ ) [19] influence the solid state structures and solution behaviour of  $LH_2^{2-tolyl}$ and LH2<sup>2,4-xylyl</sup> derived [C,N] palldacycles. Towards these goals, we describe herein the synthesis, structural aspects and solution behaviour of LH2<sup>2-tolyl</sup> and LH2<sup>2,4-xylyl</sup> derived six-membered [C,N] palladacycles (1a-d, 2a-b, 3a-d, 4 and 5) and  $LH_2^{2-tolyl}$ derived ring contracted five-membered [C,N] palladacycle, (6) and compare the structural features of these palladacycles with the corresponding palladacycles derived from  $LH_2^{2-anisyl}$ .



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# 2. Results and discussion

# 2.1. The carboxylato bridged [C,N] palladacycles (1a-1d)

 $LH_2^{2-tolyl}$  was treated with Pd(OAc)<sub>2</sub> in toluene at 70 °C for 8 h to afford **1a** in 91% yield following the C–H activation process [20–22]



Chart 1.

and the analogous reaction carried out with  $Pd(TFA)_2$  (TFA:  $OC(O)CF_3$ ) in toluene at 58 °C afforded **1b** in 81% yield. The reaction of  $LH_2^{2.4-xylyl}$  with  $Pd(OAc)_2$  and  $Pd(TFA)_2$  carried out separately in toluene at 58 °C for 8 h afforded **1c** and **1d**, respectively in 88% yield (Scheme 1).

The molecular structures **1a**, and **1c** have been determined by single crystal X-ray diffraction data and are depicted in Fig. 1. Selected bond distances and bond angles are listed in Table 1. The palladium atom is surrounded by four atoms – imine nitrogen, aryl carbon, and one oxygen atom from each of the two syn-syn bidentate bridging acetate moiety and thus possesses a slightly distorted square planar geometry. Palladacycles **1a** and **1c** possess a crystallographic  $C_2$  symmetry and a pseudo  $C_2$  symmetry, respectively that passes vertically across the Pd…Pd non-bonded axis and this arrangement affords a transoid in-in conformation. In transoid form, the imine nitrogen or metalated carbon of one six-membered "[C.N]Pd" ring is placed opposite to the identical atom in the other half of the palladacycle whereas in the cisoid form these atoms are placed on the same side. The in-in, in-out and out-out nomenclature refers to the orientation of the NH proton of one six-membered "[C,N]Pd" ring with respect to the orientation of the NH proton of the remaining six-membered "[C,N]Pd" ring.

The six-membered "[C,N]Pd" ring in **1a** and **1c** adopts a pseudo boat conformation wherein the Pd atom and the endocyclic NH nitrogen atom occupy the tips of the boat while the remaining atoms occupy the basal plane of the boat. The *o*-Me substituent



Scheme 1. Temperature: 70 °C (1a); 58 °C (1b-1d).



Fig. 1. Molecular structures of 1a and 1c at the 30% probability level. Two molecules crystallised in an asymmetric unit but only molecule 1 of 1c is shown for clarity. Hydrogen atoms except amino hydrogens and toluene in the case of 1a are omitted for clarity.

| Selected bond distances (Å) and | d bond angles | s (°) for | 1a and | 1 <b>c</b> . |
|---------------------------------|---------------|-----------|--------|--------------|
| 1a                              |               |           |        |              |

| Pd1–N1          | 2.022(2) | Pd1···Pd1  | 2.9326(7) |
|-----------------|----------|------------|-----------|
| Pd1-C19         | 1.964(3) | N1-Pd1-01  | 90.95(7)  |
| Pd1-01          | 2.134(2) | 01-Pd1-02  | 87.24(8)  |
| Pd1-O2          | 2.066(2) | C19-Pd1-O2 | 91.61(9)  |
| C10-N1          | 1.311(4) | C19-Pd1-N1 | 90.1(1)   |
| C10-N2          | 1.363(4) | N1-Pd1-O2  | 177.67(7) |
| C10-N3          | 1.346(4) | C19-Pd1-O1 | 174.55(9) |
| 1c (molecule 1) |          |            |           |
| Pd1-N1          | 2.013(5) | Pd2-N4     | 2.004(4)  |
| Pd1-C23         | 1.966(6) | Pd2-C48    | 1.953(6)  |
| Pd1-01          | 2.129(4) | Pd2-02     | 2.050(4)  |
| Pd1-03          | 2.041(4) | Pd2-04     | 2.153(4)  |
| C13-N1          | 1.282(7) | C38-N4     | 1.301(6)  |
| C13-N2          | 1.382(7) | C38-N5     | 1.361(7)  |
| C13-N3          | 1.346(8) | C38-N6     | 1.368(7)  |
|                 |          | Pd1···Pd2  | 2.983(2)  |
| 03-Pd1-01       | 86.7(2)  | C48-Pd2-O2 | 90.3(2)   |
| N1-Pd1-O3       | 175.4(2) | N4-Pd2-O4  | 92.8(2)   |
| N1-Pd1-01       | 91.4(2)  | 02-Pd2-04  | 88.0(2)   |
| C23-Pd1-O1      | 173.5(2) | N4-Pd2-O2  | 177.7(2)  |
| C23-Pd1-O3      | 90.9(2)  | C48-Pd2-O4 | 172.4(2)  |
| C23-Pd1-N1      | 90.6(2)  | C48-Pd2-N4 | 88.6(2)   |
|                 |          |            |           |

of the =NAr unit orients downward from the basal plane of the boat (i.e.  $\beta$  conformation) as analogously observed in  $[Pd\{\kappa^2(C,N)-C_6H_3(OMe)-3(NHC(NHAr)(=NAr))-2\}(\mu-OAc)]_2$  (Ar = 2-(MeO)C<sub>6</sub>H<sub>4</sub>; I) [18]. The non-bonded Pd  $\cdots$  Pd distance, 2.9326(7) Å in **1a** is comparable with that known for  $[Pd\{\kappa^2(C,N)-C_6H_4(NHC(Ph)(=NPh))-2\}(\mu-OAc)]_2$  (2.9435(4) Å) [23] but is shorter than that known for I (3.005(2) Å) [18], and **1c** (2.983(2) Å; molecule 1). This trend arises possibly due to the lesser electron richness of the palladium atom in **1a** caused by less strongly donating guanidine unit than the more electron richness of the palladium atom in **I** [18] and **1c** caused by more strongly donating guanidine units.

The Pd–O bond trans to the aryl carbon is longer than the Pd–O bond that is *trans* to the imine nitrogen in **1a** (2.134(2), 2.066(2) Å)and **1c** (2.129(4), 2.041(4); 2.153(4), 2.050(4) Å (molecule 1)) due to greater trans influence of the aryl carbon. The bond length difference between the C=N double bond and the adjacent endocyclic C–N(H) single bond ( $\Delta_{CN} = d(C-N) - d(C=N)$ ) or the adjacent exocyclic C-N(H) single bond  $(\Delta'_{CN} = d(C-N) - d(C=N))$  have been used to understand the degree of  $n-\pi$  conjugation involving the N(H) lone pair with the C=N  $\pi^*$  orbital of the imine unit [18,19,24].  $\Delta_{CN}$ : 0.035(6) Å value in **1a** is smaller than  $\Delta'_{CN}$ : 0.052(6) Å value indicating a more favourable alignment of the lone pair on the endocyclic amino nitrogen with the C=N  $\pi^*$  orbital than that on the exocyclic amino nitrogen. Further,  $\Delta_{CN}$  and  $\Delta'_{CN}$  values of **1a** are smaller than that known for LH<sub>2</sub><sup>2-tolyl</sup> ( $\Delta_{CN}$ : 0.095(6) and  $\Delta'_{CN}$ : 0.098(6) Å) [19] indicating an improved  $n-\pi$  conjugation upon palladacycle formation. The  $\Delta_{CN}$ : 0.064(11) Å value is smaller but  $\Delta'_{CN}$ : 0.100(10) Å value is comparable for the guanidine moiety bound to Pd1 in **1c** relative to that known for LH<sub>2</sub><sup>2,4-xylyl</sup> ( $\Delta_{CN}$ : 0.091(3) Å and  $\Delta'_{CN}$ : 0.108(3) Å) [19] perhaps due to subtle packing forces in the crystal lattice. The amino nitrogens in 1a and 1c are planar or nearly planar.

A variable temperature (VT) <sup>1</sup>H NMR data of **1a** indicated the presence of two species with one of them being predominant at ambient temperature. However, only one species was observed at temperatures  $\leq 253$  K (Fig. S1 in the Supplementary data). The major species in solution was assigned to the acetate bridged dimer, **1a** and the minor species was assigned to the  $\kappa^2$ -0,0'-OAc monomer **A**, illustrated in Chart 2. The <sup>1</sup>H NMR spectrum of **1a** at 5.0 mM concentration revealed two species in about 1.00:0.15 ratio but only one species was observed at 101.2 mM concentration as revealed by <sup>1</sup>H and <sup>13</sup>C NMR data. Palladacycle **1c** also



Table 2

Population of species 1 and 2 of **1c** as a function of concentration as estimated by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) data. The  $CH_3$  signals at  $\delta$  = 1.82 and 1.95 ppm were used as reference peaks to estimate the population of species 1 and species 2, respectively.

| Conc. (mM) | 5.0  | 7.8  | 21.8 | 38.7 |
|------------|------|------|------|------|
| Species 1  | 1.00 | 1.00 | 1.00 | 1.00 |
| Species 2  | 0.40 | 0.23 | 0.10 | 0.08 |

revealed concentration dependent <sup>1</sup>H NMR spectral pattern (Table 2). Thus, from the results of VT and variable concentration (VC) <sup>1</sup>H NMR studies, we suggest that species 1 corresponds to the dimer **1c** and species 2 corresponds to the monomer **B** (Chart 2).

In solution, some [C,N] palladacycles were shown to undergo the acetato ring inversion [25] or the six-membered "[C,N]Pd" ring inversion [26,27] or the latter process in conjunction with the acetato cleavage process to afford transoid in-in, transoid in-out, and transoid out-out conformers as well as monomeric pincer type and  $\kappa^2$ -0,0'-OAc palladacycles as established for I [18]. The difference in solution behaviour between 1a and 1c on the one hand and that of I [18] on the other is ascribed to higher steric bulk of o-Me group of =NAr unit in the former palladacycles compared with o-OMe group of the same unit in the latter. Further, the ability of o-OMe group of =NAr unit in I to participate in anchimeric assistance is believed to be responsible for the formation of monomeric pincer-type palladacycle in solution. Interestingly, the <sup>1</sup>H NMR spectrum of 1b and 1d revealed the presence of only one isomer in solution at ambient condition that contrasts with the <sup>1</sup>H NMR pattern of **1a** and **1c**. This could be probably ascribed to the greater reactivity of 1a and 1c towards solvents in bridge-splitting reaction to afford A and B, respectively as compared to their trifluoroacetato analogues, **1b** and **1d**.

#### 2.2. The bromo bridged [C,N] palladacycles (2a and 2b)

Palladacycles **1a** and **1c** upon metathetical reaction with excess of LiBr in aqueous ethanol at 78 °C for 8 h afforded **2a** and **2b** in 87% and 85% yield, respectively (Scheme 2). The molecular structures of **2a** and **2b** have been determined by single crystal X-ray diffraction data and are depicted in Fig. 2. Selected bond distances and bond angles are listed in Table 3.

The imine derived halo bridged six-membered [*C*,*N*] palladacycles are known to exist as *transoid* [4,28–31] and *cisoid* [15,32] conformers. Palladacycles **2a** and **2b** exist as a dimer in *transoid* form and the former possesses a crystallographic  $C_2$  symmetry that passes vertically across the centre of the puckered [Pd( $\mu$ -Br)<sub>2</sub>Pd]<sup>2+</sup> unit while the latter does not possess such symmetry. The six-



Scheme 2. (i) LiBr, EtOH-H<sub>2</sub>O (9:1), 78 °C, 8 h.

membered "[C,N]Pd" ring of two halves of the molecule and the four-membered  $[Pd(\mu-Br)_2Pd]^{2+}$  ring are puckered in the same direction in **2a** (i.e. butterfly like framework) but these rings are puckered in opposite direction in **2b** (i.e. bat like framework). The puckered conformation of the  $[Pd(\mu-Br)_2Pd]^{2+}$  ring in **2a** and **2b** versus a planar rhomboid conformation of the same unit in  $[Pd\{\kappa^2(C,N)-C_6H_3(OMe)-3(NHC(NHAr)(=NAr))-2\}(\mu-Br)]_2$  (Ar = 2-(MeO)C<sub>6</sub>H<sub>4</sub>;

**II**) [18] can be explained by invoking a greater steric bulk of the *o*-Me substituent of ==NAr unit in the former palladacycles than *o*-OMe substituent of the same unit in the latter. The dihedral angle between two PdBr<sub>2</sub> planes in **2a** ( $\phi$ : 21.77(2)°) is much smaller than that observed in **2b** ( $\phi$ : 54.94(2)°) and as a result, the non-bonded Pd…Pd distance, 3.6635(9) Å in the former is greater than the corresponding distance, 3.3804(4) Å observed in the latter. Two types of Pd–Br distances (2.4439(7), 2.5853(8) Å(**2a**), 2.4501(5), 2.5840(5) Å (**2b**)) are typical for [*C*,*N*] palladacycles.

Palladacycle **2a** was subjected to a VT <sup>1</sup>H NMR study to understand its solution behaviour. The stack plot for  $CH_3$  protons of the guanidine moiety is shown in Fig. 3. At 298 K, three peaks were observed at  $\delta$  = 1.63, 2.07 and 2.34 ppm assignable to  $CH_3$  protons of the guanidine moiety and these peaks decoalesce into six peaks ( $\delta$  = 1.61, 1.62, 2.03, 2.04, 2.30 and 2.31 ppm) at 268 K. The <sup>1</sup>H NMR pattern remains almost unaltered below 268 K. The ESI-MS mass spectrum of **2a** revealed peaks at m/z = 1464, 949 and 475 amu assignable to [trimer–Br]<sup>+</sup>, [**2a**–Br]<sup>+</sup> and [(*C*,*N*)Pd+K]<sup>+</sup> fragments, respectively (Fig. S2 in the Supplementary data). The ESI-MS mass spectrum of **2b** revealed peaks at m/z = 1592 and 1122 assignable to the [trimer–Br]<sup>+</sup> and [**2b**+Li]<sup>+</sup>, respectively. It is to be noted that the number of <sup>13</sup>C NMR signals for the aryl carbons of **2b** is greater than expected, possibly due to the presence of



Fig. 2. Molecular structures of 2a and 2b at the 30% probability level. Hydrogen atoms except amino hydrogens and solvent molecules are omitted for clarity.

96.2(1) 88.0(2)

| <b>'able 3</b><br>elected bond distances (Å) and bond angles (°) for <b>2a</b> and <b>2b</b> . |           |             |  |  |  |
|--|-----------|-------------|--|--|--|
| 2a   |           |             |  |  |  |
| Pd1-N1   | 2.036(4)  | N1-Pd1-Br1  |  |  |  |
| Pd1-C17  | 1.971(5)  | C17-Pd1-N1  |  |  |  |
| Pd1-Br1  | 2.4439(7) | C17-Pd1-Br1 |  |  |  |
| Dd1_Br1  | 2 5853(8) | C17_Dd1_Br1 |  |  |  |

| Pul-Bri    | 2.4439(7) | CI/-Pui-Bri | 91.5(2)  |
|------------|-----------|-------------|----------|
| Pd1-Br1    | 2.5853(8) | C17-Pd1-Br1 | 175.8(2) |
| C1-N1      | 1.301(7)  | Br1-Pd1-Br1 | 84.28(2) |
| C1-N2      | 1.365(7)  | Pd1-Br1-Pd1 | 93.47(2) |
| C1-N3      | 1.346(7)  | C1-N1-Pd1   | 122.0(3) |
| Pd1…Pd1    | 3.6635(9) | C1-N3-C16   | 124.5(5) |
| N1-Pd1-Br1 | 173.3(1)  |             |          |
| 2b         |           |             |          |
| Pd1-C19    | 1.979(4)  | C19-Pd1-N1  | 88.6(2)  |
| Pd1-N1     | 2.037(3)  | C19-Pd1-Br1 | 93.9(1)  |
| Pd1-Br1    | 2.4501(5) | C19-Pd1-Br2 | 172.8(1) |
| Pd1-Br2    | 2.5840(5) | N1-Pd1-Br1  | 173.2(1) |
| N1-C1      | 1.298(5)  | Br2-Pd1-Br1 | 82.12(2) |
| N2-C1      | 1.353(5)  | N1-Pd1-Br2  | 96.02(9) |
| N3-C1      | 1.354(5)  | Pd2-Br1-Pd1 | 84.06(2) |
| Pd2-N4     | 2.039(3)  | Pd1-Br2-Pd2 | 84.22(2) |
| Pd2-C44    | 1.988(4)  | C44-Pd2-N4  | 89.0(2)  |
| Pd2-Br1    | 2.5961(5) | C44-Pd2-Br1 | 173.1(1) |
| Pd2-Br2    | 2.4552(6) | N4-Pd2-Br2  | 173.9(1) |
| N4-C26     | 1.293(5)  | Br1-Pd2-Br2 | 81.77(2) |
| N5-C26     | 1.372(5)  | N4-Pd2-Br1  | 95.28(9) |
| N6-C26     | 1.353(5)  | C44-Pd2-Br2 | 94.5(1)  |
| Pd1···Pd2  | 3.3804(4) |             |          |
|            |           |             |          |

![](_page_4_Figure_3.jpeg)

**Fig. 3.** A VT <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of **2a** shown for  $CH_3$  protons of the guanidine moiety. The  $\bullet$  symbol indicates proton signal of adventitious H<sub>2</sub>O.

two species in solution. From the results of NMR and mass spectral data, we conclude that **2a** and **2b** exist as dimer in the solid state but as a mixture of a dimer and presumably a trimer (**C** and **D**) in solution (Chart 3).

![](_page_4_Figure_6.jpeg)

#### 2.3. Monomeric [C,N] palladacycles (3a-d, 4, 5 and 6)

A suspension of 2a in CH<sub>2</sub>Cl<sub>2</sub> was treated with 2,6-lutidine, 3,5-lutidine, 2,4-lutidine, <sup>t</sup>BuN=C and PTA (1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane) in 1:1 (Pd:L) mole ratio at ambient temperature to afford 3a-3c, 4, and 5, respectively in 83-88% yield. Similarly, 2b was treated with 2,6-lutidine in 1:1 (Pd:L) mole ratio in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature to afford 3d in 93% yield (Scheme 3, step i). Palladacycle 2a was treated with XyN=C in 1:1 (Pd:L) mole ratio in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature to afford  $[Pd{\kappa^2(C,N)-C_6H_3Me-3(NHC(NHAr)(=NAr))-}$ 2}Br(C=NXy)] (Ar = 2-MeC<sub>6</sub>H<sub>4</sub>; Xy = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) but this attempt proved futile and the starting materials remained largely unreacted. The difference in reactivity pattern between <sup>t</sup>BuN=C and XyN=C toward 2a could be attributed to the higher nucleophilicity of the former [33] that enables cleavage of **2a** to afford **4**. The insertion reaction of **2a** with XyN≡C carried out in 1:2 (Pd:L) mole ratio in CH<sub>2</sub>Cl<sub>2</sub> at ambient condition for 24 h led to the formation of a ring contracted five-membered [C,N] palladacycle, 6 in 93% yield. This reaction appears to proceed through a sevenmembered  $[(C,N)PdBr(C \equiv NXy)]$  intermediate that upon ring contraction followed by amine-imine tautomerisation afforded 6 as previously proposed in the formation of  $[Pd{\kappa^2(C,N)} C = NXy(C_6H_3(OMe)-4)-2(N = C(NHAr)_2)-3Br(C = NXy)$ (Ar = 2-(MeO)C<sub>6</sub>H<sub>4</sub>; **III**) [18] (Scheme 3, step ii).

The molecular structures of 3a, 3c, 3d, 4-6 have been determined by single crystal X-ray diffraction data and are depicted in Fig. 4. Selected bond distances and bond angles are listed in Tables 4-6. The palladium atom in these palladacycles revealed a somewhat distorted square planar geometry. The Lewis base is coordinated to the palladium atom in *cis* relation with respect to the Pd-C bond. The molecular structures of imine derived six-membered [C,N] palladacycles of the type [(C,N)PdX(L)] (L = pyridine, and phosphine [4,34–38]), and  $[Pd{\kappa^2(C,N)-C_6H_3(OMe)-$ 3(NHC(NHAr)(=NAr))-2Br(C=NXy)] (Ar = 2-(MeO)C<sub>6</sub>H<sub>4</sub>; **IV** [18]) are known to contain the Lewis base cis to the Pd-C bond due to antisymbiosis. However, an unusual trans configuration was observed for the palladium atom in  $[Pd{\kappa^2(C,N)-C_6H_3(OMe)-$ 3(NHC(NHAr)(=NAr))-2Br(L) (Ar = 2-(MeO)C<sub>6</sub>H<sub>4</sub>; L = 2,6- $Me_2C_5H_3N$  (Va), 2,4- $Me_2C_5H_3N$  (Vb)) [18] and such configuration was explained by invoking relative hardness/softness of the donor atoms surrounding the palladium and its antisymbiotic behaviour [39]. The greater steric bulk of the aryl moiety of the =NAr unit in 3a, 3c, and 3d than that present in Va and Vb could be the reason for the reversal of stereochemistry around the palladium atom rather than antisymbiosis. There would be an unfavourable steric

ArHN Br (i) HN Bridge-splitting reaction Me Ar R L 2-MeC<sub>6</sub>H<sub>4</sub> Н 2,6-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N ArHN 3a 3b 2-MeC<sub>6</sub>H<sub>4</sub> Н 3,5-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N CH<sub>2</sub>Cl<sub>2</sub> HI 3c 2-MeC<sub>6</sub>H<sub>4</sub> Н 2,4-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N RT, 24 h 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> 3d Me 2,6-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N Me 4 2-MeC<sub>6</sub>H<sub>4</sub> <sup>t</sup>BuN≡C н 5 Н PTA 2-MeC<sub>6</sub>H<sub>4</sub> NHAr ArHN Ar R Me 2a 2-MeC<sub>6</sub>H<sub>4</sub> Н Br 2b 2,4-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> Me (ii) Insertion reaction ≡NXv X١  $Ar = 2-MeC_6H_4$ 6  $Xy = 2,6-Me_2C_6H_3$ 

![](_page_5_Figure_2.jpeg)

![](_page_5_Figure_3.jpeg)

Fig. 4. Molecular structures of 3a, 3c, 3d, and 4–6 at the 30% probability level. Hydrogen atoms except amino hydrogens and methanol in the case of 5 are omitted for clarity.

repulsion between the *o*-Me group of lutidine and that of the =NAr moiety in a hypothetical *trans* isomer of **3a**, **3c**, and **3d** and hence *cis* configuration is preferred. The *cis* configuration of the palladium atom in **4** and **5** could be ascribed largely to antisymbiosis, as analogously suggested for **IV** [18]. The Lewis base in **4**, and **5** could be softer than bromine and hence prefers to lie *trans* to the harder imine nitrogen atom.

The Pd–Br distance is longer while the Pd–N(lutidine) distance is shorter in **3a** (Pd–Br: 2.5491(2) Å; Pd–N: 2.048(1) Å), **3c** (Pd–Br: 2.5601(5) Å; Pd–N: 2.048(3) Å), and **3d** (Pd–Br: 2.535(1) Å; Pd–N: 2.035(6) Å) than those observed in **Va** (Pd–Br: 2.441(6) Å; Pd–N: 2.173(4) Å (molecule 1)) and **Vb** (Pd–Br: 2.446(5) Å; Pd–N: 2.160(3) Å) [18] as the bromine atom is *trans* to the softer aryl carbon in the former set of palladacycles. The six-membered "[*C*,*N*]Pd"

| Table 4   |  |
|---|--|
| Selected bond distances (Å) and bond angles (deg) for <b>3a</b> , <b>3c</b> , and <b>3d</b> . |  |

| 3a      |           |             |           |
|---------|-----------|-------------|-----------|
| Pd1-N1  | 2.034(1)  | C17-Pd1-N1  | 88.53(6)  |
| Pd1-C17 | 1.985(2)  | C17-Pd1-N4  | 91.03(6)  |
| Pd1-N4  | 2.048(1)  | N1-Pd1-Br1  | 95.03(4)  |
| Pd1-Br1 | 2.5491(2) | N4-Pd1-Br1  | 85.50(4)  |
| N1-C1   | 1.311(2)  | N1-Pd1-N4   | 178.92(5) |
| N2-C1   | 1.361(2)  | C17-Pd1-Br1 | 173.51(5) |
| 30      |           |             |           |
| Pd1-N1  | 2.039(3)  | C17-Pd1-N1  | 89.7(2)   |
| Pd1-C17 | 1.997(4)  | C17-Pd1-N4  | 92.4(2)   |
| Pd1-N4  | 2.048(3)  | N1-Pd1-Br1  | 94.38(9)  |
| Pd1–Br1 | 2.5601(5) | N4-Pd1-Br1  | 83.54(9)  |
| N1-C1   | 1.308(5)  | N1-Pd1-N4   | 177.5(1)  |
| N2-C1   | 1.356(5)  | C17-Pd1-Br1 | 175.6(1)  |
| N3-C1   | 1.343(5)  |             |           |
| 3d      |           |             |           |
| Pd1-N1  | 2.037(6)  | N1-Pd1-C19  | 89.0(3)   |
| Pd1-C19 | 2.046(8)  | N1-Pd1-Br1  | 93.7(2)   |
| Pd1-N4  | 2.035(6)  | N4-Pd1-C19  | 91.1(3)   |
| Pd1-Br1 | 2.535(1)  | N4-Pd1-Br1  | 86.2(2)   |
| N1-C1   | 1.29(1)   | N4-Pd1-N1   | 179.0(3)  |
| N2-C1   | 1.38(1)   | C19-Pd1-Br1 | 175.0(2)  |
| N3-C1   | 1.37(1)   |             |           |
|         | . ,       |             |           |

Table 5

Selected bond distances (Å) and bond angles (°) for 4 and 5.

| 4  |  |  |   |
|--|--|--|---|
| Pd1-N1   | 2.049(3)   | C17-Pd1-N1   | 89.1(1)   |
| Pd1-C17  | 2.004(3)   | C23-Pd1-C17  | 89.6(2)   |
| Pd1-C23  | 1.933(4)   | C23-Pd1-Br1  | 85.2(1)   |
| Pd1-Br1  | 2.5273(5)  | N1-Pd1-Br1   | 96.09(7)  |
| N1-C1  | 1.294(4)   | C23-Pd1-N1   | 175.2(1)  |
| N2-C1  | 1.372(4)   | C17-Pd1-Br1  | 174.8(1)  |
| N3-C1  | 1.357(4)   | N4-C23-Pd1   | 177.7(4)  |
| N4-C23   | 1.136(5)   |  |   |
|  |  |  |   |
| 5  |  |  |   |
| <b>5</b><br>Pd1–N1   | 2.111(4)   | C17-Pd1-N1   | 88.1(2)   |
| <b>5</b><br>Pd1–N1<br>Pd1–C17  | 2.111(4)<br>2.007(5)   | C17-Pd1-N1<br>C17-Pd1-P1   | 88.1(2)<br>93.2(1)  |
| <b>5</b><br>Pd1–N1<br>Pd1–C17<br>Pd1–P1                                | 2.111(4)<br>2.007(5)<br>2.247(1)   | C17–Pd1–N1<br>C17–Pd1–P1<br>N1–Pd1–Br1   | 88.1(2)<br>93.2(1)<br>94.2(1)                                     |
| <b>5</b><br>Pd1–N1<br>Pd1–C17<br>Pd1–P1<br>Pd1–Br1                     | 2.111(4)<br>2.007(5)<br>2.247(1)<br>2.522(1)                                     | C17-Pd1-N1<br>C17-Pd1-P1<br>N1-Pd1-Br1<br>P1-Pd1-Br1                             | 88.1(2)<br>93.2(1)<br>94.2(1)<br>85.45(4)                         |
| <b>5</b><br>Pd1–N1<br>Pd1–C17<br>Pd1–P1<br>Pd1–Br1<br>N1–C1            | 2.111(4)<br>2.007(5)<br>2.247(1)<br>2.522(1)<br>1.313(7)                         | C17–Pd1–N1<br>C17–Pd1–P1<br>N1–Pd1–Br1<br>P1–Pd1–Br1<br>N1–Pd1–P1                | 88.1(2)<br>93.2(1)<br>94.2(1)<br>85.45(4)<br>166.1(1)             |
| <b>5</b><br>Pd1-N1<br>Pd1-C17<br>Pd1-P1<br>Pd1-Br1<br>N1-C1<br>N2-C1   | 2.111(4)<br>2.007(5)<br>2.247(1)<br>2.522(1)<br>1.313(7)<br>1.357(6)             | C17–Pd1–N1<br>C17–Pd1–P1<br>N1–Pd1–Br1<br>P1–Pd1–Br1<br>N1–Pd1–P1<br>C17–Pd1–Br1 | 88.1(2)<br>93.2(1)<br>94.2(1)<br>85.45(4)<br>166.1(1)<br>175.6(1) |
| 5<br>Pd1-N1<br>Pd1-C17<br>Pd1-P1<br>Pd1-Br1<br>N1-C1<br>N2-C1<br>N3-C1 | 2.111(4)<br>2.007(5)<br>2.247(1)<br>2.522(1)<br>1.313(7)<br>1.357(6)<br>1.363(7) | C17-Pd1-N1<br>C17-Pd1-P1<br>N1-Pd1-Br1<br>P1-Pd1-Br1<br>N1-Pd1-P1<br>C17-Pd1-Br1 | 88.1(2)<br>93.2(1)<br>94.2(1)<br>85.45(4)<br>166.1(1)<br>175.6(1) |

Table 6

Selected bond distances (Å) and bond angles (°) for 6.

|            | 0         |             |           |
|------------|-----------|-------------|-----------|
| Pd1-N1     | 2.090(2)  | C32-Pd1-C23 | 97.7(1)   |
| Pd1-C23    | 2.011(3)  | C32-Pd1-Br1 | 84.99(8)  |
| Pd1-Br1    | 2.5980(3) | C32-Pd1-N1  | 177.0(1)  |
| Pd1-C32    | 1.944(3)  | C23-Pd1-Br1 | 168.69(9) |
| N1-C1      | 1.318(3)  | C1-N1-C16   | 123.5(2)  |
| N3-C1      | 1.363(3)  | C1-N1-Pd1   | 123.4(2)  |
| N2-C1      | 1.353(3)  | C16-N1-Pd1  | 108.8(2)  |
| N4-C23     | 1.259(4)  | C23-N4-C24  | 125.4(3)  |
| N5-C32     | 1.150(3)  | N5-C32-Pd1  | 166.7(2)  |
| C23-Pd1-N1 | 81.11(9)  | C32-N5-C33  | 173.0(3)  |
| N1-Pd1-Br1 | 96.73(5)  |             |           |
|            |           |             |           |

ring in **3a**, **3d**, **4** and **5** revealed a pseudo boat  $\beta$  conformation that contrasts with the pseudo boat  $\alpha$  conformation observed for the same ring in **IV**, **Va** and **Vb**. The structural features of **6** are identical with those found in **III** [18].

The <sup>1</sup>H NMR spectrum of **3a**, **3b** and **3d** revealed the presence of two isomers in about 3.0:1.0, 3.0:1.5 and 3.0:0.6 ratio, respectively as estimated from the intensities of  $CH_3$  protons of lutidine and those of the guanidine moiety. Further, **3a** and **3d** revealed two signals for  $CH_3$  protons of 2,6-lutidine that indicates a pseudo boat

#### Table 7

Population of two isomers of **3d** as a function of concentration as estimated by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) data. The  $CH_3$  signals of 2,6-lutidine at  $\delta$  = 2.67 and 2.97 ppm were used as reference peaks to estimate the population of isomer 2 and isomer 1, respectively.

| Conc. (mM) | 6.4  | 32.2 | 58.0 | 83.9 | 109.7 | 364.0 |
|------------|------|------|------|------|-------|-------|
| Isomer 1   | 1.00 | 1.00 | 1.00 | 1.00 | 1.00  | 1.00  |
| Isomer 2   | 0.08 | 0.11 | 0.12 | 0.13 | 0.14  | 0.28  |

conformation for the six-membered "[C,N]Pd" ring in solution too as previously shown for **Va** [18] and the related palladacycles [25]. The CH<sub>3</sub> protons of 3,5-lutidine in **3b** are isochronous as these protons are placed farther away from the centre of the boat.

A variable temperature <sup>1</sup>H NMR study carried out on the sample of **3d** did not indicate any spectral change throughout the temperature range studied. (Figs. S3 and S4 in the Supplementary data). Presumably, the six-membered "[C,N]Pd" ring inversion occurs faster than the NMR timescale due to the presence of sterically more hindered = NAr unit. Palladacycle **3d** was subjected to a VC <sup>1</sup>H NMR study and the results are listed in Table 7. The population of isomer 2 increases although not smoothly upon increasing the concentration of the analyte. The population of the isomer at a particular concentration appears to depend upon the subtle balance between the steric effect and noncovalent interactions. It may be that noncovalent interactions such as intermolecular N-H-.-Br and C-H...Br hydrogen bonding is predominant over steric effect in the solid-state to afford the isomer 2 (i.e.  $\beta$  conformer) but such interactions play no significant role in dilute solution and hence the population of solution conformer is solely determined by steric factor (Fig. S5 in the Supporting Information). The role of noncovalent interactions becomes increasingly important upon increasing the concentration of the analyte as the molecules approach close to one another and hence the population of isomer 2 increases relative to isomer 1. The isomer 2 could be a kinetic rather than a thermodynamic product of the crystallisation process [40]. Based on the VC <sup>1</sup>H NMR results, we assign isomer 1 to the  $\alpha$  conformer and the isomer 2 to the  $\beta$  conformer in solution.  $\alpha$  and  $\beta$  conformers of 3a, 3b and 3d differ from each other in the orientation of o-Me group of the =NAr unit with respect to the basal plane of the boat (Scheme 4).

The <sup>1</sup>H NMR spectrum of **3c** revealed the presence of four isomers in about 3.0:2.3:0.5:0.5 ratios as estimated from the <sup>1</sup>H NMR integrals of  $CH_3$  protons of 2,4-lutidine. One pair of isomers is assigned to  $\alpha$  and  $\beta$  conformers and the other pair is assigned to  $\alpha'$  and  $\beta'$  conformers.  $\alpha$  and  $\beta$  conformers can interconvert via a six-membered "[*C*,*N*]Pd" ring inversion as do  $\alpha'$  and  $\beta'$  conformers.  $\alpha$  and  $\alpha'$  conformers and  $\beta$  and  $\beta'$  conformers interconvert via the Pd–N(lutidine) bond rotation or dissociation followed by recoordination of lutidine. Ryabov and co-worker have shown that the second pathway is unlikely for the related six-membered [*C*,*N*] palladacycle [41], although such pathway is usually proposed to explain the formation of two isomers of five-membered [*C*,*N*] palladacycles of the type [(*C*,*N*)PdCl(L)] [42,43]. Thus, we suggest that  $\alpha \leftrightarrow \alpha'$  or  $\beta \leftrightarrow \beta'$  interconversion possibly occurs through the Pd–N(lutidine) bond rotation.

Unlike **Va** and **Vb**,  $\alpha$  and  $\beta$  conformers of **3a**, **3b** and **3d** can also interconvert via =N-C(Ar) single bond rotation [44,45] but this process is unlikely in the latter palladacycles due to steric factor. However,  $\alpha$  and  $\beta$  conformers and  $\alpha'$  and  $\beta'$  conformers can interconvert through a planar intermediate via the six-membered "[*C*,*N*]Pd" ring inversion as discussed for **Va** [18]. The effective steric bulk of *o*-Me substituent of =NAr moiety in **3a-3d** is greater than that of *o*-OMe substituent of the same unit in **Va**, and **Vb** and hence the former palladacycles are less stable in the planar conformation than the latter.

![](_page_7_Figure_2.jpeg)

**Scheme 4.** Conformational equilibria of **3a–3d**. (i) Six-membered "[*C*,*N*]Pd" ring inversion, (ii) Pd–N(lutidine) bond rotation. The palladated aryl ring is indicated as C=C for clarity.

The bridge-splitting reaction of five-membered platinacycles of the type  $[(C,N)Pt(\mu-X)]_2$  with Lewis base, L was shown to afford a kinetically controlled product *trans*-[(C,N)PtX(L)] (L = pyridine [46]) and in some cases *trans*-[(C,N)PtX(L)] was shown to rearrange to a thermodynamically controlled *cis*-[(C,N)PtX(L))] (L = 2,6-luti-dine and PPh<sub>3</sub>) upon standing or upon heating [47,48]. Thus, we suggest that **Va** and **Vb** are the kinetic products of the bridge-splitting reaction involving **II** and lutidine [18] whereas **3a**, **3c** and **3d** are the thermodynamic products of such reaction involving **2a** or **2b** and lutidine.

# 3. Conclusions

Palladacycles **1a** and **1c** were shown to exist as a dimer in the solid state but as a mixture of predominantly a dimer and a monomer in solution. Palladacycles **2a** and **2b** were shown to exist as a dimer in the solid state but as a mixture of a dimer and a trimer in solution. The presence of two species in solution was ascribed to the cleavage of OAc/Br bridges in **1a**, **1c**, **2a**, and **2b** by solvent molecule. The stereochemical outcome of the bridge-splitting reaction was shown to be controlled by steric factor or antisymbiosis. The number of solution conformers of *cis*-[(*C*,*N*)PdBr(L)] depends not only upon the shape and symmetry but also on the  $\sigma$ -donor/ $\pi$ -acceptor characteristics of the Lewis base, L.

#### 4. Experimental

# 4.1. General remarks

LH<sub>2</sub><sup>2-tolyl</sup>, LH<sub>2</sub><sup>2,4-xylyl</sup> and PTA were prepared following the reported procedures [19,49]. The instrumental details pertinent to IR, NMR, mass spectral and microanalytical data are as reported in our previous publications [18,50]. For few samples, <sup>1</sup>H and <sup>13</sup>C

NMR data were acquired on Jeol ECX 400 NMR spectrometer operating at 400, 100.81 MHz, respectively. The <sup>13</sup>C NMR assignments of **1a**, **2b**, and **4** were made with the aid of DEPT and HETCOR NMR data (Figs. S6–S14 in the Supplementary data). The <sup>31</sup>P NMR data of **5** was recorded on Jeol ECX 400 NMR spectrometer operating at 161.8 MHz with 85% H<sub>3</sub>PO<sub>4</sub> as the external standard. The experimental procedures for **1a–1d** are analogous to that described previously for **I**, those of **2a** and **2b** are analogous to that described previously for **Va** while that of **6** is analogous to that described previously for **III** [18].

# 4.2. Synthesis, analytical and spectroscopic data of [C,N] palladacycles

#### 4.2.1. Palladacycle 1a

Yield: 91%. Mp(DSC): 196.30 °C. Anal. Calc. for Pd<sub>2</sub>C<sub>48</sub>H<sub>50</sub>N<sub>6</sub>O<sub>4</sub>·C<sub>7</sub>H<sub>8</sub> (Mw: 1079.95): C, 61.17; H, 5.41; N. 7.78. Found: C, 60.86; H, 5.42; N, 7.62%. IR (KBr, cm<sup>-1</sup>): v(NH) 3426 m, 3397 m; v(C=N) 1629 vs; v<sub>a</sub>(OCO) 1575 vs, v<sub>s</sub>(OCO) 1404 s. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 5.0 mM): dimer, **1a**: monomer,  $\mathbf{A} \approx 1.00:0.15; \ \delta \ 1.37 \ (s, \ 6H, \ CH_3, \ 1a), \ 1.69 \ (s, \ 6H, \ CH_3, \ 1a), \ 1.76$ (s, 3H, CH<sub>3</sub>, **A**), 1.86 (s, 6H, CH<sub>3</sub>, **1a**), 1.94, 2.21 (each s,  $2 \times 3H$ , CH<sub>3</sub>, A), 2.53 (s, 6H, CH<sub>3</sub>, 1a), 2.55 (s, 3H, CH<sub>3</sub>, A), 5.36 (s, 3H, NH), 6.09 (s, 3H, NH), 6.47 (dd, J<sub>HH</sub> = 7.8; 2.0 Hz, 3H, ArH), 6.82, 6.83 (br, 3H, ArH), 6.91-6.93 (m, 6H, ArH), 6.99-7.03 (m, 6H, ArH), 7.10–7.23 (m, 12H, ArH), 7.65–7.67 (m, 3H, ArH). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 101.2 mM): dimer, **1a**; δ 1.37 (s, 6H, CH<sub>3</sub>), 1.69, 1.85, 2.53 (each s,  $6 \times 3H$ ,  $CH_3$ ), 5.35 (s, 2H, NH), 6.09 (s, 2H, NH), 6.49 (br, 2H, ArH), 6.82 (br, 2H, ArH), 6.92 (br, 2H, ArH), 7.02 (br, 2H, ArH), 7.16 (br, 12H, ArH), 7.68 (br, 2H, ArH). <sup>13</sup>C NMR (100.81 MHz, CDCl<sub>3</sub>, 101.2 mM): dimer, **1a**; δ 17.5, 19.3, 23.7 (CH<sub>3</sub>), 119.0 (C), 120.5 (CH), 121.6 (C), 125.8 (CH), 126.2 (CH), 127.2 (CH), 127.3 (CH), 128.1 (CH), 131.4 (CH), 131.5 (CH), 134.3 (C), 134.4 (CH), 134.6 (C), 135.3 (C), 143.6 (C), 144.0 (C), 179.6 (OC(O)). Note: Only three carbon peaks were observed for CH<sub>3</sub> carbon rather than the expected four peaks due to overlap at  $\delta$  = 17.5 ppm and only 16 carbon resonances were observed for ArC and C=N carbons rather than the expected 19 peaks, presumably due to overlapping peaks. TOF MS<sup>+</sup>, m/z (relative intensity%), [ion]: 929 (90), [M–OAc]<sup>+</sup>; 516 (62), [monomer+Na]<sup>+</sup>; 464 (50),  $[monomer-2 Me]^+; 434 (67), [(C,N)Pd]^+; 328 (100), [LH_2^{2-tolyl}-H]^+.$ Crystals suitable for X-ray diffraction data were grown from CH<sub>2</sub>Cl<sub>2</sub>/toluene mixture at ambient condition over a period of several days to afford **1a** C<sup>7</sup>H<sub>8</sub> as shiny greenish yellow crystals.

#### 4.2.2. Palladacycle 1b

Yield: 81%. *Anal.* Calc. for  $Pd_2C_{48}H_{44}N_6O_4F_6$ .0.20  $CH_2Cl_2$  (Mw: 1112.74): C, 52.03; H, 4.02; N, 7.55. Found: C, 52.05; H, 4.03; N, 7.33%. IR (KBr, cm<sup>-1</sup>): v(NH) 3424 m, 3378 m;  $v_a(OCO)$  1682 vs; v(C=N) 1635 vs;  $v_s(OCO)$  1542 s;  $v(CF_3)$  1207 vs, 1148 s. <sup>1</sup>H NMR (300 MHz, CDCl\_3):  $\delta$  1.75, 1.88, 2.50 (each s,  $6 \times 3H$ ,  $CH_3$ ), 5.44 (s, 2H, NH), 6.23 (d,  $J_{HH}$  = 7.8 Hz, 2H, ArH), 6.26 (s, 2H, NH), 6.84 (d,  $J_{HH}$  = 6.9 Hz, 2H, ArH), 6.90–6.99 (br, m, 6H, ArH), 7.05 (t,  $J_{HH}$  = 7.5 Hz, 2H, ArH), 7.20, 7.22 (br, 8H, ArH), 7.47 (d,  $J_{HH}$  = 7.2 Hz, 2H, ArH). <sup>13</sup>C NMR (75.5 MHz, CDCl\_3):  $\delta$  17.4, 17.5, 18.9 (CH<sub>3</sub>), 115.2 (q,  $^{1}J_{CF}$  = 288.8 Hz, CF<sub>3</sub>), 118.4, 119.6, 121.1, 125.9, 126.6, 126.7, 127.0, 127.1, 127.5, 128.5, 131.6, 131.8, 133.3, 133.6, 134.1, 134.2, 135.4, 142.2, 144.4 (ArC and C=N), 163.9 (q,  $^{2}J_{CF}$  = 37.5 Hz, OC(O)). <sup>19</sup>F NMR (282.4 MHz, CDCl\_3):  $\delta$  –74.6.

#### 4.2.3. Palladacycle 1c

Yield: 88%. *Anal.* Calc. for  $Pd_2C_{54}H_{62}N_6O_4$  (Mw: 1071.96): C, 60.50; H, 5.83; N, 7.84. Found: C, 60.61; H, 5.82; N, 7.82%. IR (KBr, cm<sup>-1</sup>): v(NH) 3429 m, 3396 m; v(C=N) 1635 vs;  $v_a(OCO)$  1592 vs,  $v_s(OCO)$  1413 s. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 5.0 mM): dimer (**1**c): monomer (**B**)  $\approx$  1.00:0.40;  $\delta$  1.37, 1.66 (s, 2 × 6H, CH<sub>3</sub>, **1**c),

1.73 (s, 3H, CH<sub>3</sub>, **B**), 1.82 (s, 6H, CH<sub>3</sub>, **1c**), 1.95, 2.15 (each s, 2 × 3H, CH<sub>3</sub>, **B**), 2.22 (s, 6H, CH<sub>3</sub>, **1c**), 2.23 (s, 3H, CH<sub>3</sub>, **B**), 2.29 (s, 6H, CH<sub>3</sub>, **1c**), 2.32, 2.34 (each s, 2 × 3H, CH<sub>3</sub>, **B**), 2.40 (s, 6H, CH<sub>3</sub>, **1c**), 2.49 (br, 6H, CH<sub>3</sub>, 1c; 3H, CH<sub>3</sub>, B), 5.27 (s, 2H, NH, 1c), 5.48 (s, 1H, NH, B), 6.00 (s, 2H, NH, 1c), 6.40 (d,  $J_{\rm HH}$  = 7.7 Hz, 2H, ArH, 1c), 6.51 (s, 1H, NH, **B**), 6.66–6.70 (br, 5H, ArH), 6.77 (d, J<sub>HH</sub> = 8.0 Hz, 2H, ArH), 6.86 (s, 1H, ArH), 6.93 (d, J<sub>HH</sub> = 8.1 Hz, 2H, ArH), 6.97 (d, J<sub>HH</sub> = 11.7 Hz, 4H, ArH), 7.03–7.20 (br, 6H, ArH), 7.45 (s, 2H, ArH). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 90.6 mM): dimer, **1c**:  $\delta$  17.4, 17.5, 19.2, 20.9, 21.1, 23.6, 26.9 (CH<sub>3</sub>), 118.4, 121.2, 126.3, 126.5, 126.9, 127.2, 127.7, 129.0, 131.9, 132.1, 132.2, 134.1, 134.7, 135.0, 135.2, 137.7, 141.2, 144.0 (ArC and C=N), 179.2 (OC(O)). Note: Only 18 carbon resonances were observed for ArC and C=N carbons rather than the expected 19 peaks, presumably due to overlapping peaks. ESI-MS<sup>+</sup>, m/z (relative intensity %), [ion]: 1013  $(74), [M-OAc]^+; 517 (100), [(C,N)Pd+K]^+; 370 (91), [LH_2^{2,4-xylyl}-H]^+.$ Crystals suitable for X-ray diffraction data were grown from toluene at ambient condition over a period of several days to afford **1c** as greenish yellow crystals.

#### 4.2.4. Palladacycle 1d

Yield: 88%. *Anal.* Calc. for  $Pd_2C_{54}H_{56}N_6O_4F_6 \cdot 0.5C_7H_8$  (Mw: 1225.97): C, 56.33; H, 4.93; N, 6.85. Found: C, 56.29; H, 5.32; N, 6.71%. IR (KBr, cm<sup>-1</sup>): v(NH) 3427 m, 3372 m;  $v_a(OCO)$  1674 vs; v(C=N) 1635 vs;  $v_s(OCO)$  1531 s;  $v(CF_3)$  1205 vs, 1145 s. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.73, 1.84, 2.21, 2.32, 2.39, 2.46 (each s, 12 × 3H, *CH*<sub>3</sub>), 5.38 (s, 2H, N*H*), 6.09 (d,  $J_{HH}$  = 7.8 Hz, 2H, *ArH*), 6.20 (s, 2H, N*H*), 6.69 (t,  $J_{HH}$  = 9.0 Hz, 2H, *ArH*), 6.76 (s, 4H, *ArH*), 6.95–7.02 (m, 6H, *ArH*), 7.17 (d,  $J_{HH}$  = 7.2 Hz, 2H, *ArH*). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  17.3, 17.4, 18.9, 20.8, 20.9, 21.0 (CH<sub>3</sub>), 115.2 (q, <sup>1</sup> $J_{CF}$  = 288.2 Hz, *CF*<sub>3</sub>), 118.1, 119.2, 126.0, 126.9, 127.1, 127.7, 127.9, 129.8, 131.0, 131.6, 132.0, 132.3, 133.8, 134.0, 135.2, 136.2, 138.4, 139.7, 144.4 (ArC and *C*=N), 163.5 (q, <sup>2</sup> $J_{CF}$  = 37.8 Hz, OC(O)). <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>):  $\delta$  –74.8.

#### 4.2.5. Palladacycle 2a

Yield: 87%. *Anal.* Calc. for  $Pd_2C_{44}H_{44}N_6Br_2\cdot 2.5CHCl_3$  (Mw: 1327.97): C, 42.06; H, 3.53; N, 6.33. Found: C, 41.68/41.88; H, 3.49/3.36; N, 6.26/6.28%. IR (KBr, cm<sup>-1</sup>): v(NH) 3422 m, 3385 m; v(C=N) 1625 vs. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.63, 2.07, 2.34 (each s, 3 × 3H, CH<sub>3</sub>), 5.94 (br), 5.99 (br), 6.34 (br), 6.55 (t,  $J_{HH} = 7.2$  Hz), 6.69 (d,  $J_{HH} = 7.2$  Hz), 7.11–7.33 (br m) (ArH and NH). The <sup>13</sup>C NMR spectrum for **2a** was not recorded owing to its poor solubility in common deuterated solvents. ESI-MS<sup>+</sup>, m/z (relative intensity %), [ion]: 1464 (100), [**C**–Br]<sup>+</sup>; 949 (28), [**2a**–Br]<sup>+</sup>; 475 (30), [(*C*,*N*)Pd+K]<sup>+</sup>; 328 (95) [LH<sub>2</sub><sup>2-tolyl</sup>–H]<sup>+</sup>. Suitable crystals for X-ray diffraction study were grown from CHCl<sub>3</sub> at ambient temperature over a period of several days to afford **2a**·3CHCl<sub>3</sub> as cuboidal yellow crystals.

#### 4.2.6. Palladacycle 2b

Yield: 85%. *Anal.* Calc. for Pd<sub>2</sub>C<sub>50</sub>H<sub>56</sub>N<sub>6</sub>Br<sub>2</sub>·2.5 CH<sub>2</sub>Cl<sub>2</sub> (Mw: 1326.03): C, 47.55; H, 4.64; N, 6.34. Found: C, 47.76; H, 4.66; N, 6.55%. IR (KBr, cm<sup>-1</sup>): *v*(NH) 3409 m, 3386 m; *v*(C=N) 1626 vs. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): *δ* 1.60, 2.03, 2.15 (each s,  $6 \times 3$ H, CH<sub>3</sub>), 2.23, 2.27, 2.31 (each br,  $6 \times 3$ H, CH<sub>3</sub>), 5.79, 5.85 (br, 2H, ArH), 6.21, 6.48 (each s,  $2 \times 2$ H, NH), 6.95–7.17 (br m, 14H, ArH). <sup>13</sup>C NMR (100.81 MHz, CDCl<sub>3</sub>): *δ* 16.9, 17.7, 19.1, 20.7, 21.1 (CH<sub>3</sub>), 120.3, 120.5, 123.8, 124.0, 124.4, 126.8, 126.9 (CH), 127.3 (CH), 128.4 (CH), 130.6, 130.8 (br), 131.4, 131.8 (CH), 131.9 (CH), 132.1 (CH), 132.3 (CH), 133.9, 134.3 (br), 135.3, 135.6, 136.0, 138.2 (CH), 138.7, 141.3, 141.5, 141.8, 146.7 (ArC and C=N). *Note:* Only five carbon resonances were observed for CH<sub>3</sub> carbons rather than the expected six peaks due to overlap at *δ* = 21.1 ppm. ESI-MS<sup>+</sup>, *m/z* (relative intensity %), [ion]: 1592 (33), [**D**–Br]<sup>+</sup>; 1122 (48), [**2b**+Li]<sup>+</sup>; 519 (39), [(C,N)Pd+K]<sup>+</sup>, 370 (100) [LH<sub>2</sub><sup>2.4-xylyl</sup>-H]<sup>+</sup>.

Suitable crystals for X-ray diffraction data were grown from  $CH_2Cl_2/toluene$  mixture at ambient temperature over a period of several days to afford **2b**·C<sub>7</sub>H<sub>8</sub> as cuboidal yellow crystals.

#### 4.2.7. Palladacycle 3a

Yield: 88%. *Anal.* Calc. for PdC<sub>29</sub>H<sub>31</sub>N<sub>4</sub>Br (Mw: 621.91): C, 56.01; H, 5.02; N, 9.01. Found: C, 55.84; H, 5.20; N, 9.08%. IR (KBr, cm<sup>-1</sup>): ν(NH) 3426 m, 3405 m; ν(C=N) 1623 vs. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): α:β conformers ≈ 3.0:1.0; δ 1.57 (s, 3H, CH<sub>3</sub>, β), 1.69 (s, 3H, CH<sub>3</sub>, α), 2.10 (s, 3H, CH<sub>3</sub>, β), 2.13 (s, 3H, CH<sub>3</sub>, α), 2.26 (s, 3H, CH<sub>3</sub>, α), 2.48 (s, 3H, CH<sub>3</sub>, β), 2.52 (s, 3H, 2.6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, β), 2.67 (s, 3H, 2.6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, α), 2.97 (s, 3H, 2.6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, β), 3.34 (s, 3H, 2.6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, α), 5.76 (s, 1H, NH, α), 5.84 (d, J<sub>HH</sub> = 7.5 Hz, 1H, ArH, β), 5.93 (br, 1H, ArH), 6.07 (s, 1H, NH, β), 6.24 (d, J<sub>HH</sub> = 7.8 Hz, 1H, ArH, α), 6.30 (br, 1H, NH, β), 6.40 (d, J<sub>HH</sub> = 7.2 Hz, 1H, ArH, β), 6.45 (s, 1H, NH, α), 6.55–6.74 (m, 5H, ArH), 6.91–7.00 (m, 3H, ArH), 7.14–7.36 (m, 14H, ArH), 7.47–7.54 (m, 1H, ArH), 8.00 (d, J<sub>HH</sub> = 6.6 Hz, 1H, ArH, α). ESI-MS<sup>+</sup>, m/z (relative intensity %), [ion]: 541 (27), [M–Br]<sup>+</sup>; 475 (100), [(C,N)Pd+K]<sup>+</sup>; 328 (99), [LH<sub>2</sub><sup>2-tolyl</sup>–H]<sup>+</sup>.

#### 4.2.8. Palladacycle 3b

Yield: 85%. Anal. Calc. for PdC<sub>29</sub>H<sub>31</sub>N<sub>4</sub>Br 0.75 C<sub>7</sub>H<sub>8</sub> (Mw: 691.02): C, 59.53; H, 5.40; N, 8.11. Found: C, 59.60; H, 5.57; N, 8.10%. IR (KBr, cm<sup>-1</sup>): v(NH) 3426 m, 3378 m; v(C=N) 1624 vs. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\alpha$ : $\beta$  conformers  $\approx$  3.0:1.5;  $\delta$  1.65 (s, 3H, CH<sub>3</sub>, β), 1.70 (s, 3H, CH<sub>3</sub>, α), 2.06 (s, 3H, CH<sub>3</sub>, β), 2.11 (s, 6H, 3,5-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, β), 2.18 (s, 3H, CH<sub>3</sub>, β), 2.22 (s, 6H, 3,5- $(CH_3)_2C_5H_3N$ ,  $\alpha$ ), 2.36, 2.44 (s, 2 × 3H,  $CH_3$ ,  $\alpha$ ), 5.79 (s, 1H, NH,  $\beta$ ), 6.08 (s, 1H, NH,  $\alpha$ ), 6.12 (d, J<sub>HH</sub> = 7.8 Hz, 1H, ArH,  $\alpha$ ), 6.44 (s, 1H, NH,  $\alpha$ ), 6.49 (t, J<sub>HH</sub> = 7.5 Hz, 2H, ArH,  $\alpha$ ), 6.67–6.80 (m, 2H, ArH; 1H, NH,  $\beta$ ), 6.94 (t, J<sub>HH</sub> = 7.5 Hz, 1H, ArH,  $\beta$ ), 7.06–7.40 (m, 15H, ArH), 7.46 (d,  $J_{\rm HH}$  = 7.5 Hz, 1H, ArH,  $\alpha$ ), 7.81 (s, 1H, 4-H, 3,5- $Me_2C_5H_3N$ ,  $\alpha$ ), 8.09 (dd,  $J_{HH}$  = 9.0; 3.0 Hz, 1H, 4-H, 3,5- $Me_2C_5H_3N$ ,  $\beta$ ), 8.24 (br, 2H, 2-H, 3,5-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\beta$ ), 8.42 (s, 1H, 2-H, 3,5- $Me_2C_5H_3N$ ,  $\alpha$ ), 8.49 (s, 1H, 2-H, 3,5- $Me_2C_5H_3N$ ,  $\beta$ ). ESI- $MS^+$ , m/z (relative intensity %), [ion]: 475 (94), [(C,N)Pd+K]<sup>+</sup>; 328 (100), [LH<sub>2</sub><sup>2-</sup> <sup>tolyl</sup>-Hl<sup>+</sup>.

#### 4.2.9. Palladacycle 3c

Yield: 88%. *Anal.* Calc. for PdC<sub>29</sub>H<sub>31</sub>N<sub>4</sub>Br (Mw: 621.91): C, 56.01; H, 5.02; N, 9.01. Found: C, 56.03/56.04; H, 5.28/5.17; N, 8.99/9.01%. IR (KBr, cm<sup>-1</sup>): v(NH) 3418 m, 3314 m; v(C=N) 1623 vs. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\alpha$ : $\beta$ :  $\alpha'$ : $\beta'$  conformers  $\approx$  3.0:2.3:0.5:0.5;  $\delta$  1.69 (br s, 12H, CH<sub>3</sub>,  $\alpha$ ,  $\beta$ ,  $\alpha'$ ,  $\beta'$ ), 2.11 (br s, 12H, CH<sub>3</sub>,  $\alpha$ ,  $\beta$ ,  $\alpha'$ ,  $\beta'$ ), 2.18 (s, 3H, CH<sub>3</sub>,  $\alpha'$ ), 2.23 (s, 3H, CH<sub>3</sub>,  $\beta'$ ), 2.26 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\alpha'$ ), 2.31 (s, 6H, CH<sub>3</sub>,  $\alpha$ ,  $\beta$ ), 2.42 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\alpha'$ ), 2.46 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\beta$ ), 2.48 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\alpha'$ ), 2.54 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\alpha'$ ), 2.79 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\beta$ ), 3.06 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\alpha'$ ), 3.16 (s, 3H, 2.4-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N,  $\alpha$ ), 5.73, 5.86, 6.00 (t, J<sub>HH</sub> = 6.3 Hz), 6.08 (d, J<sub>HH</sub> = 5.1 Hz), 6.44, 6.48, 6.51, 6.63, 6.70, 6.71, 6.73 (br), 6.82–6.99 (m), 7.12, 7.17 (d, J<sub>HH</sub> = 7.2 Hz), 7.29, 7.47 (d, J<sub>HH</sub> = 7.8 Hz), 7.80 (d, J<sub>HH</sub> = 6.0 Hz), 8.10 (m), 8.49 (d, J<sub>HH</sub> = 5.7 Hz), 8.85 (d, J<sub>HH</sub> = 5.4 Hz) (ArH and NH).

# 4.2.10. Palladacycle 3d

Yield: 93%. *Anal.* Calc. for PdC<sub>32</sub>H<sub>37</sub>N<sub>4</sub>Br (Mw: 663.99): C, 57.88; H, 5.62; N, 8.44. Found: C, 58.13; H, 5.41; N, 8.60%. IR (KBr, cm<sup>-1</sup>): ν(NH) 3412 m, 3300 w; ν(C=N) 1626 vs. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): α:β conformers ≈ 3.0:0.6; δ 1.66, 1.89, 2.04 (each s, 3 × 3H, CH<sub>3</sub>, α), 2.07, 2.16, 2.20, 2.23 (each s, 4 × 3H, CH<sub>3</sub>, β), 2.30 (br s, 6H, CH<sub>3</sub>, α, β), 2.33, 2.41 (each s, 2 × 3H, CH<sub>3</sub>, α), 2.52 (s, 3H, CH<sub>3</sub>, β), 2.67 (s, 3H, 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, β), 2.97 (s, 3H, 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, α), 3.32 (s, 3H, 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, β), 3.33 (s, 3H, 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N, α), 5.58 (s, 1H, NH, α), 5.66 (s, 1H, NH, β), 5.98 (s, 1H, NH, α), 6.08 (d, J<sub>HH</sub> = 8.2, 1H, ArH, β), 6.33 (s, 1H, NH, β), 6.35 (s, 1H, Ar*H*, *α*), 6.50 (s, 1H, Ar*H*, *α*), 6.52 (s, 1H, Ar*H*, *β*), 6.63 (d,  $J_{\text{HH}}$  = 7.4, 1H, Ar*H*, *β*), 6.97, 6.99 (each s, 2H, Ar*H*), 7.02 (s, 2H, Ar*H*), 7.04 (s, 2H, Ar*H*), 7.07, 7.08 (br m, 3H, Ar*H*), 7.13 (d,  $J_{\text{HH}}$  = 7.3, 1H, Ar*H*), 7.34 (s, 3H, Ar*H*), 7.36 (s, 2H, Ar*H*), 7.50 (t,  $J_{\text{HH}}$  = 7.6, 1H, Ar*H*), 7.81 (s, 1H, Ar*H*). TOF MS<sup>+</sup>, m/z (relative intensity %), [ion]: 583 (100), [M–Br]<sup>+</sup>; 477 (33), [M–Br,L]<sup>+</sup>; 370 (33) [LH<sub>2</sub><sup>2,4-xylyl</sup>–H]<sup>+</sup>. Suitable crystals for X-ray diffraction data were grown from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane mixture at ambient temperature over a period of several days to afford **3d** as yellow crystals.

# 4.2.11. Palladacycle 4

To a suspension of 2a (200 mg, 0.194 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added a solution of <sup>t</sup>BuN=C (34 mg, 0.41 mmol) made in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The resulting mixture was stirred at room temperature for 2 h. During the course of the reaction the solid dissolved to afford a clear solution. The solution was concentrated under vacuum to about 5 mL and layered with *n*-hexane to afford **4** as green crystals after several days. Yield: 88% (205 mg, 0.343 mmol). Mp: 159 °C (dec.). Anal. Calc. for PdC<sub>27</sub>H<sub>31</sub>N<sub>4</sub>Br (Mw: 597.89): C, 54.24; H, 5.22; N, 9.37. Found: C, 54.03; H, 5.27; N, 9.43%. IR (KBr, cm<sup>-1</sup>): v(NH) 3418 m, 3326 w; v(C=N) 2215 vs; v(C=N) 1621 vs. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.50 (s, 9H, CH<sub>3</sub>), 1.67, 2.11, 2.34 (each s,  $3 \times 3H$ ,  $CH_3$ ), 6.01, 6.38 (each s,  $2 \times 1H$ , NH), 6.72 (t, J<sub>HH</sub> = 7.3, 1H, ArH), 6.82 (d, J<sub>HH</sub> = 7.3, 1H, ArH), 7.12-7.16 (m, 2H, ArH), 7.28-7.34 (m, 7H, ArH). <sup>13</sup>C NMR (100.81 MHz. CDCl<sub>3</sub>): δ 17.2, 17.7, 19.1, 30.0 (CH<sub>3</sub>), 57.7 (Me<sub>3</sub>CN≡C), 122.2 (CH), 122.6, 126.3 (CH), 127.0 (CH), 127.8 (CH), 128.1 (CH), 128.2 (Me<sub>3</sub>CN=C), 128.7 (CH), 129.0 (CH), 131.0 (CH), 131.6, 131.8 (CH), 134.1, 134.3, 134.8, 136.5, 139.4 (CH), 144.0, 146.7 (ArC and C=N). Note: Only 18 carbon resonances were observed for ArC and *C*=N carbons rather than the expected 19 peaks, due to two overlapping peaks at  $\delta$  = 126.3 ppm. TOF MS<sup>+</sup>, m/z (relative intensity %), [ion]: 583 (100), [M-Me]<sup>+</sup>.

#### 4.2.12. Palladacycle 5

A solution of PTA (30 mg, 0.19 mmol) in  $CH_2Cl_2$  (10 mL) was added to the suspension of **2a** (100 mg, 0.097 mmol) in  $CH_2Cl_2$  (10 mL) and the resulting mixture was stirred at ambient

Crystallographic and refinement data for **1a** C<sub>7</sub>H<sub>8</sub>. **1c**. **2a** 3CHCl<sub>3</sub>. **2b** C<sub>7</sub>H<sub>8</sub> and **3a**.

temperature for 24 h. The solution was concentrated under vacuum to about 5 mL, layered with MeOH and stored at ambient temperature for several days to afford 5.2CH<sub>3</sub>OH as vellow cuboidal crystals. Yield: 83% (118 mg, 0.160 mmol). Anal. Calc. for PdC<sub>28</sub>H<sub>34</sub>N<sub>6</sub>PBr·2CH<sub>3</sub>OH (Mw: 735.99): C, 48.96; H, 5.75; N, 11.42. Found: C, 48.82; H, 6.00; N, 11.62%. IR (KBr, cm<sup>-1</sup>): v(NH) 3414 m, 3361 w; v(C=N) 1614 vs. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 1.64, 2.05, 2.12 (each s,  $3 \times 3H$ ,  $CH_3$ ), 4.28, 4.45 (each s,  $6 \times 2H$ ,  $CH_2$ ), 6.08, 6.27 (each s, 2 × 1H, NH), 6.75–6.80 (m, 2H, ArH), 7.08–7.12 (m, 2H, ArH), 7.16–7.18 (m, 1H, ArH), 7.23 (d, J<sub>HH</sub> = 7.5, 1H, ArH), 7.27 (s, 1H, ArH), 7.28-7.30 (m, 3H, ArH), 7.35 (d,  $J_{\rm HH}$  = 6.8, 1H, ArH). <sup>13</sup>C NMR (100.81 MHz, CDCl<sub>3</sub>):  $\delta$  16.9, 17.8, 19.1 (CH<sub>3</sub>), 53.2 (d,  $J_{CP}$  = 17.3 Hz, PCH<sub>2</sub>), 73.2 (d,  $J_{CP}$  = 6.7 Hz, NCH<sub>2</sub>), 122.8 (d, J<sub>CP</sub> = 4.8 Hz), 123.3, 123.4, 126.1 (d, J<sub>CP</sub> = 8.6 Hz), 126.6, 127.8, 128.1, 129.1 (d,  $J_{CP}$  = 19.2 Hz), 131.2, 131.8, 131.9, 133.4, 134.6, 134.7, 136.2, 136.6, 137.6 (d,  $I_{CP}$  = 14.4 Hz), 143.8, 148.4 (ArC and C=N). <sup>13</sup>P NMR (CDCl<sub>3</sub>, 161.8 MHz):  $\delta$  -48.8. TOF MS<sup>+</sup>, *m/z* (relative intensity %), [ion]: 673 (15), [M+H]<sup>+</sup>; 629 (30), [M+2H-3Me]<sup>+</sup>; 591 (100), [M-Br]<sup>+</sup>; 458 (10), [M-PTA, Br+Na]<sup>+</sup>, 328 (72)  $[LH_2^{2-tolyl}-H]^+$ . Suitable crystals for X-ray diffraction study were grown from CH<sub>3</sub>OH at ambient temperature over a period of several days to afford **5** CH<sub>3</sub>OH as irregular yellow crystals.

#### 4.2.13. Palladacycle 6

Yield: 93%. *Anal.* Calc. for PdC<sub>40</sub>H<sub>40</sub>N<sub>5</sub>Br (Mw: 777.11): C, 61.82; H, 5.19; N, 9.01. Found: C, 62.18; H, 5.19; N, 8.89%. IR (KBr, cm<sup>-1</sup>): v(NH) 3382 m; v(C=N) 2177 vs; v(C=NXy) 1628 s; v(C=N) 1568 vs. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.06 (br, 6H, 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 2.16 (s, 6H, 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=C), 2.31 (s, 3H, CH<sub>3</sub>), 2.43, 2.76 (each br, 2 × 3H, CH<sub>3</sub>), 5.92 (br, 1H, NH), 6.49 (br, 1H, ArH), 6.53 (t,  $J_{HH}$  = 7.2 Hz, 1H, ArH), 6.92–7.28 (br m, 14H, ArH), 7.69 (d,  $J_{HH}$  = 7.2 Hz, 1H, ArH), 9.84 (br, 1H, NH). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>):  $\delta$  17.9 (br, CH<sub>3</sub>), 18.3, 18.6, 20.0 (br, CH<sub>3</sub>), 121.9 (br), 122.9 (br), 123.4 (br), 124.7 (br), 125.2 (br), 126.0, 126.7, 127.3, 128.2 (br), 128.8, 129.0, 129.2, 130.6, 132.9, 134.6, 134.8 (br), 141.0 (br), 142.9 (br), 149.8 (ArC), 151.6 (Pd-C=N), 154.2 (Pd-N=C), 177.2 (Pd-C=N). Note: Only four carbon resonances were observed for CH<sub>3</sub> carbon rather than the expected five peaks and

|  | <b>1a</b> ·C <sub>7</sub> H <sub>8</sub>                                      | 1c                       | 2a 3CHCl <sub>3</sub>  | 2 <b>b</b> ·C <sub>7</sub> H <sub>8</sub>                                      | 3a  |
|--|---|--------------------------|--|--|---|
| Formula  | Pd <sub>2</sub> C <sub>55</sub> H <sub>58</sub> N <sub>6</sub> O <sub>4</sub> | $Pd_2C_{54}H_{62}N_6O_4$ | Pd <sub>2</sub> C <sub>47</sub> H <sub>47</sub> N <sub>6</sub> Br <sub>2</sub> Cl <sub>8</sub> | Pd <sub>2</sub> C <sub>57</sub> H <sub>64</sub> N <sub>6</sub> Br <sub>2</sub> | PdC <sub>29</sub> H <sub>31</sub> N <sub>4</sub> Br |
| Fw   | 1079.87   | 1071.90                  | 1387.58  | 1205.76  | 621.89  |
| T (K)  | 298(2)  | 298(2)                   | 298(2)   | 298(2)   | 100(2)  |
| λ (Å)  | 0.71073   | 0.71073                  | 0.71073  | 0.71073  | 0.71073   |
| Crystal system                                 | monoclinic  | triclinic                | monoclinic   | triclinic  | triclinic   |
| Space group                                    | C2/c  | ΡĪ                       | C2/c   | ΡĪ   | ΡĪ  |
| a (Å)  | 15.225(3)   | 12.297(7)                | 22.684(2)  | 13.0583(5)   | 11.4763(6)  |
| b (Å)  | 17.592(3)   | 17.823(11)               | 18.244(1)  | 14.5003(6)   | 12.3050(6)  |
| <i>c</i> (Å)                                   | 19.150(5)   | 25.043(15)               | 14.705(1)  | 17.1901(8)   | 12.3960(7)  |
| α (°)  | 90.00   | 78.499(13)               | 90.00  | 113.085(4)   | 93.515(2)   |
| β (°)  | 104.281(3)  | 75.943(12)               | 116.011(11)  | 95.030(3)  | 116.767(3)  |
| γ (°)  | 90.00   | 79.822(12)               | 90.00  | 110.903(4)   | 115.592(2)  |
| $V(Å^3)$                                       | 4970.7(17)  | 5169(5)                  | 5469.3(8)  | 2697.4(3)  | 1336.56(14)   |
| Ζ  | 4   | 4                        | 4  | 2  | 2   |
| $D_{\text{calc}} (\text{g cm}^{-3})$           | 1.443   | 1.377                    | 1.685  | 1.485  | 1.545   |
| F(000)   | 2216  | 2208                     | 2744   | 1220   | 628   |
| $\mu (\mathrm{mm}^{-1})$                       | 0.775   | 0.745                    | 2.597  | 2.190  | 2.213   |
| $\theta$ range (°)                             | 1.80-27.00  | 1.56-26.37               | 2.84-26.37   | 2.89-26.37   | 1.94-35.49  |
| Reflections measured                           | 5458  | 21048                    | 5584   | 11016  | 12063   |
| Reflections used                               | 4433  | 11924                    | 4807   | 8634   | 10324   |
| Parameters                                     | 308   | 1229                     | 296  | 612  | 322   |
| $R[I > 2\sigma(I)]$                            |   |                          |  |  |   |
| $R_1$  | 0.0343  | 0.0662                   | 0.0554   | 0.0405   | 0.0311  |
| wR <sub>2</sub>                                | 0.0964  | 0.1001                   | 0.1644   | 0.0983   | 0.0864  |
| Goodness of fit on $F^2$                       | 1.051   | 1.021                    | 1.034  | 1.054  | 1.154   |
| Largest difference in peak/hole (e Å $^{-3}$ ) | 0.716/-0.675  | 0.696/-0.451             | 1.098/-1.200   | 0.705/-0.550   | 1.406/-1.158  |

Table 8

| Table 9 | ) |
|---------|---|
|---------|---|

Crystallographic and refinement data for 3c, 3d, 4, 5 CH<sub>3</sub>OH and 6.

| Complex  | 3c  | 3d  | 4   | <b>5</b> · CH <sub>3</sub> OH                         | 6   |
|--|---|---|---|---|---|
| Formula  | PdC <sub>29</sub> H <sub>31</sub> N <sub>4</sub> Br | PdC <sub>32</sub> H <sub>37</sub> N <sub>4</sub> Br | PdC <sub>27</sub> H <sub>31</sub> N <sub>4</sub> Br | PdC <sub>29</sub> H <sub>38</sub> N <sub>6</sub> OBrP | PdC <sub>40</sub> H <sub>40</sub> N <sub>5</sub> Br |
| Fw   | 621.89  | 663.97  | 597.87  | 703.93  | 777.08  |
| T (K)  | 298(2)  | 100(2)  | 100(2)  | 100(2)  | 298(2)  |
| λ (Å)  | 0.71073   | 0.71073   | 0.71073   | 0.71073   | 0.71073   |
| Crystal system                                 | triclinic   | triclinic   | triclinic   | monoclinic  | triclinic   |
| Space group                                    | ΡĪ  | ΡĪ  | ΡĪ  | $P2_1/c$  | ΡĪ  |
| a (Å)  | 11.4400(5)  | 12.313(3)   | 11.6871(4)  | 10.613(5)   | 10.7869(2)  |
| b (Å)  | 11.6168(6)  | 12.510(3)   | 11.8770(5)  | 12.422(5)   | 12.8400(3)  |
| c (Å)  | 12.7373(6)  | 12.585(3)   | 11.9081(6)  | 22.387(5)   | 14.0246(3)  |
| α (°)  | 83.097(2)   | 67.563(3)   | 109.233(4)  | 90.000(5)   | 99.3450(10)   |
| β (°)  | 66.736(2)   | 62.364(3)   | 116.846(4)  | 91.834(5)   | 100.9230(10)  |
| γ (°)  | 62.235(2)   | 70.746(4)   | 99.067(3)   | 90.000(5)   | 104.8270(10)  |
| V (Å <sup>3</sup> )                            | 1371.82(11)   | 1559.5(6)   | 1297.14(13)   | 2949.9(19)  | 1797.69(7)  |
| Ζ  | 2   | 2   | 2   | 4   | 2   |
| $D_{\text{calc}} (\text{g cm}^{-3})$           | 1.506   | 1.414   | 1.531   | 1.585   | 1.436   |
| F(000)   | 628   | 676   | 604   | 1432  | 792   |
| $\mu$ (mm <sup>-1</sup> )                      | 2.156   | 1.902   | 2.277   | 2.072   | 1.662   |
| $\theta$ range (°)                             | 1.75-30.03  | 1.90-27.70  | 2.97-26.37  | 1.82-27.00  | 1.52-29.13  |
| Reflections measured                           | 7942  | 7356  | 5305  | 6437  | 9559  |
| Reflections used                               | 3977  | 4965  | 4305  | 5274  | 7210  |
| Parameters                                     | 319   | 356   | 304   | 353   | 431   |
| $R[I > 2\sigma(I)]$                            |   |   |   |   |   |
| $R_1$  | 0.0484  | 0.0737  | 0.0350  | 0.0469  | 0.0369  |
| wR <sub>2</sub>                                | 0.0922  | 0.1728  | 0.0973  | 0.1350  | 0.0868  |
| Goodness of fit on F <sup>2</sup>              | 0.957   | 1.131   | 1.029   | 1.248   | 1.010   |
| Largest difference in peak/hole ( $e A^{-3}$ ) | 0.609/-0.437  | 1.630/-2.304  | 0.792/-1.289  | 2.561/-1.608  | 1.098/-1.200  |

19 carbon resonances were observed for ArC rather than the expected 26 peaks presumably due to overlapping peaks. ESI-MS<sup>+</sup>, m/z (relative intensity %), [ion]: 778 (100),  $[M+H]^+$ ; 732 (45),  $[M-3Me]^+$ ; 696 (83),  $[M-Br]^+$ ; 565 (40)  $[(C,N)Pd+H]^+$ . Crystals suitable for X-ray diffraction data were grown from CH<sub>2</sub>Cl<sub>2</sub>/toluene mixture at ambient condition over a period of several hours.

#### 4.3. Crystal structure determinations

Suitable crystals of 1a·C<sub>7</sub>H<sub>8</sub>, 1c, 2a·3CHCl<sub>3</sub>, 2b·C<sub>7</sub>H<sub>8</sub>, 3a, 3c, 3d, 4, 5-CH<sub>3</sub>OH and 6 for X-ray diffraction study were carefully selected after examination under an optical microscope and mounted on the goniometer head with a paraffin oil coating. The unit cell parameters and intensity data for 1a C7H8, 1c, 3c and 6 were collected at 298 K and those of 3a, 3d, 4 and 5 CH<sub>3</sub>OH were collected at 100 K using a Bruker SMART APEX CCD diffractometer equipped with a fine focus Mo Ko X-ray source (50 kV, 40 mA). Intensity data of suitably sized crystals of 2a·3CHCl<sub>3</sub> and 2b·C<sub>7</sub>H<sub>8</sub> were collected at 298 K on Oxford Xcalibur S diffractormeter (4-circle kappa goniometer, Sapphire-3 CCD detector, omega scans, graphite monochromator, and a single wavelength Enhance X-ray source with Mo Ka radiation). The details pertinent to data acquisition, data reduction, absorption correction, structure solution and refinement are as reported in our previous publication [50]. The X-ray crystallographic parameters, details of data collection and structure refinement are listed in Tables 8 and 9.

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#### Appendix A. Supplementary data

CCDC 859650-859659 contain the supplementary crystallographic data for 1a C7H8, 1c, 2a 3CHCI3, 2b C7H8, 3a, 3c, 3d, 4, 5-CH<sub>3</sub>OH and 6. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2012.06.077.

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