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# Palladium(II) and palladium(II)-silver(I) complexes with N-heterocyclic carbene and zwitterionic thiolate mixed ligands: synthesis, structural characterization and catalytic properties<sup>†</sup>

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Integration of geometrically rigid Pd(II), a coordinatively monotonous N-heterocyclic carbene1,3-10 dimethylimidazoline-2-ylidene (IMe), and а flexible zwitterionic thiolate 4-(trimethylammonio)benzenethiolate (Tab) affords a class of Pd-IMe-Tab complexes with various nuclearities, namely, trans-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)<sub>2</sub> (2, mononuclear), cis-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)(Cl) (3a, cis-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> MeCN (3b·MeCN, mononuclear), mononuclear)  $[Pd_2(IMe)_4(Tab)_2](PF_6)_4 \cdot 2MeCN$  (4.2MeCN, dinuclear) and  $[Pd_4(IMe)_4(Tab)_6](OTf)_6(Cl)_2$  (5, 15 tetranuclear). Further presence of Ag(I) in the assembly provides a heterometallic octanuclear cluster of  $[Pd_4Ag_4(IMe)_8(Tab)_{10}](PF_6)_{12}$  (6). Compounds 2-6 are formed by the reaction of trans-Pd(IMe)\_2Cl<sub>2</sub> (1) with various additional reagents via different reaction pathways. These compounds are characterized by means of FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR, ESI-MS, elemental analysis and X-ray crystallography. Notably, the skeleton of compound 5 features a  $[Pd_4S_4]$  parallelogram wherein each of the four Pd(II) centers bisects  $_{20}$  the edge defined by the S atoms. The main skeleton of compound **6** is an oval-shaped Pd<sub>4</sub>Ag<sub>4</sub>S<sub>10</sub> unit, featuring an edge-fused norbornane-like (Pd2Ag4S6) framework appended by two additional PdS2 motifs at the polar positions. Compounds 5 and 6 also feature Pd···Pd (5), Pd···Ag and Ag···Ag (6) interactions. Compound 5 as a representative example is highly effective in catalyzing Suzuki-Miyaura coupling in water, highlighting the potential of applying this type of homo- and heterometallic clusters as catalysts for

25 organic transformations in environmentally benign media.

#### Introduction

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Transition metal NHC complexes have gained intense interest in the last few decades as a superior class of catalysts for organic transformations,<sup>1</sup> as well as other applications in materials <sup>30</sup> science and pharmaceutical industry.<sup>2</sup> These hot trends arise from the facile preparation and derivation of the NHC precursors, either on the skeletons or the pendant arms to tune their donation strength or stereochemistry.<sup>3</sup> Functional groups such as -OR, -NR, -PR and -SR on the pendant arms serve to elevate structural

<sup>35</sup> complexity to form di-, tri-and tetra-nuclear motifs.<sup>4</sup> Further structural complexity is however hindered by the preferable C, X (X = O, N, P and S) chelation.<sup>5</sup>

We herein report that, by the assembly of Pd(II) or Pd(II)/Ag(I) with two separate functionalities, *viz.* a simple NHC (IMe) and a <sup>40</sup> zwitterionic thiolate ligand (Tab,<sup>6</sup> Chart 1), we can readily achieve increased structural diversity and complexity by taking advantage of the flexible coordination patterns of S atom of the Tab ligand. Tab is a non-ordous zwitterionic thiolate ligand bearing a quaternary ammonium cationic center. The polar nature

45 of such a ligand endows stability of the coordination compounds

in polar solvents such as H2O. In recent years, we have also demonstrated that Tab is capable of supporting diverse clusters, such as  $[Ag_{14}(\mu_6-S)(Tab)_{12}(PPh_3)_8](PF_6)_{12}$  $[Bi_{5}(Tab)_{18}](PF_{6})_{7}(NO_{3})_{8}] \cdot 6MeCN,^{6b}$ and  $M_4(\mu _{50}$  Tab)<sub>6</sub>(Tab)<sub>4</sub>](PF<sub>6</sub>)<sub>8</sub>·S (M = Zn, S = DMF·4H<sub>2</sub>O; M = Cd, S = DMF 5H<sub>2</sub>O).<sup>8</sup> In the present study, by using *trans*-Pd(IMe)<sub>2</sub>Cl<sub>2</sub> (1) as the precursor complex, its complexation with Tab in the absence/presence of additional Ag(I) source resulted in a diverse class of homo- and hetero-nuclear molecular entities, including 55 mononuclear *trans*-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)<sub>2</sub> (2), dinuclear  $[Pd_2(IMe)_4(Tab)_2](PF_6)_4 \cdot 2MeCN$ (4·2MeCN), tetranuclear  $[Pd_4(IMe)_4(Tab)_6](OTf)_6(Cl)_2$ (5) and octanuclear  $[Pd_4Ag_4(IMe)_8(Tab)_{10}](PF_6)_{12}$  (6). In addition, we also isolated *cis*-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)(Cl) (3a)and cis-60 [Pd(IMe)2(Tab)2](PF6)2 MeCN (3b MeCN) as by-products during the isolation of 2 and 4 2MeCN. The  $Pd_4$  cluster of 5 as a representative example is efficient in promoting Suzuki-Miyaura coupling in water, highlighting the potential of using this class of S-based compounds for organic transformations in

65 environmentally benign solvents.

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#### Chart 1



#### Experimental

General procedures. TabHPF<sub>6</sub><sup>9</sup> and trans-Pd(IMe)<sub>2</sub>Cl<sub>2</sub> (1)<sup>10</sup> were obtained through the literature methods. Tab was obtained 5 from the reaction of TabHPF<sub>6</sub> with Et<sub>3</sub>N in MeCN followed by filtration and dried in vacuo. All the solvents were pre-dried over activated molecular sieves. Other chemicals and reagents were obtained from commercial sources and used as received. Elemental analyses for C, H and N were performed on a Carlo-10 Erba CHNO-S microanalyzer. IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000–400 cm<sup>-1</sup>). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at ambient temperature on a Varian UNITY plus-600, 400 or 300 spectrometer. Electrospray ion mass spectra (ESI-MS) were 15 performed on an Agilent 1200/6200 mass spectrometer using MeCN as the mobile phase.

Preparation of trans-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)<sub>2</sub> (2) and cis-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)(Cl) (3a). Adding AgOTf (51 mg, 0.2 mmol) to a solution of Tab (50 mg, 0.3 mmol) in MeOH (3 mL) 20 resulted in a colourless solution. Mixing this colourless solution with a CH<sub>2</sub>Cl<sub>2</sub> (2 mL) solution containing 1 (37 mg, 0.1 mmol) with stirring yielded a muddy yellow solution after 1 h which was filtered. Carefully layering 15 mL of Et<sub>2</sub>O onto the filtrate provided yellow block crystals of 2 in several days, accompanied 25 by а few colourless block crystals of cis-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)(Cl) (3a). The crystals were collected by filtration and washed thoroughly with Et<sub>2</sub>O before drying in vacuo. Yield: 10 mg (11% based on Pd). Anal. Calcd. for C<sub>30</sub>H<sub>42</sub>N<sub>6</sub>O<sub>6</sub>F<sub>6</sub>S<sub>4</sub>Pd (+5H<sub>2</sub>O): C 35.28, H 5.13, N 8.23; found: C 30 35.25, H 5.09, N 8.13. IR (KBr disk): 3452 (m), 3161 (w), 3131 (w), 3103 (w), 3046 (w), 2940 (w), 1637 (m), 1572 (w), 1499 (w), 1480 (m), 1422 (w), 1402 (w), 1384 (m), 1354 (w), 1270 (s), 1226 (m), 1164 (m), 1150 (m), 1120 (m), 1088 (w), 1028 (s), 1006 (m), 961 (w), 944 (w), 839 (w), 748 (w), 724 (w), 692 (m),  $_{35}$  636 (s), 572 (w), 518 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.25 (d, J = 8.7 Hz, 4H, CH in Tab), 7.14 (d, J = 8.7 Hz, 4H, CH in Tab), 6.92 (s, 4H, CH in IMe), 3.85 (s, 12H, CH<sub>3</sub> in IMe), 3.42 (s, 18H, CH<sub>3</sub> in Tab). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>, ppm):  $\delta$ 175.08 (s, C<sub>carbene</sub> in IMe), 150.65 (s, C-N in Ph of Tab), 40 142.17 (s, CH in Tab), 133.80 (s, C-S of Tab), 122.21 (d, J = 10.6

Hz, CH in IMe), 118.17 (d, J = 5.9 Hz, CH in Tab), 56.25 (d, J = 18.7 Hz, CH<sub>3</sub> in Tab), 36.97 (d, J = 18.9 Hz, CH<sub>3</sub> in IMe).

Preparation of [Pd<sub>2</sub>(IMe)<sub>4</sub>(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·2MeCN (4·2MeCN) and cis-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·MeCN (3b·MeCN). Treating a 45 suspension of TabHPF<sub>6</sub> (94 mg, 0.3 mmol) in MeOH (3 mL) with Et<sub>3</sub>N (1.25 mL) yielded a colourless clear solution. A separate portion of clear solution of 1 (37 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was then introduced. Stirring the mixture for 1 h gave rise to yellow precipitate. The precipitate was filtered off, re-dissolved

50 in MeCN (4 mL) and filtered again. Diffusing Et<sub>2</sub>O (15 mL) slowly into the filtrate provided light vellow block crystals of 4 2MeCN after two weeks, accompanied by trace amount of cis-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> MeCN (**3b** MeCN). Yield: 26.5 mg (35%) based on Pd). Anal. Calcd. for C<sub>42</sub>H<sub>64</sub>N<sub>12</sub>F<sub>24</sub>P<sub>4</sub>S<sub>2</sub>Pd<sub>2</sub>: C 30.19, H

- 55 3.87, N 9.27; found: C 30.23, H 4.07, N 9.26. IR (KBr disk): 3440 (s), 2985 (w), 2052 (w), 1692 (m), 1489 (w), 1384 (m), 1226 (w), 1128 (m), 1005 (w), 843 (s), 784 (w), 749 (w), 617 (w), 558 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.60 (dd, J = 21.8, 8.8 Hz, 8H, CH in Tab), 7.26 (s, 8H, CH in IMe), 3.85
- 60 (s, 24H, CH<sub>3</sub> in IMe), 3.51 (s, 18H, CH<sub>3</sub> in Tab). <sup>13</sup>C NMR (151 MHz, DMSO-d<sub>6</sub>, ppm): δ 158.57 (s, C<sub>carbene</sub> in IMe), 145.40 (s, C-N in Ph of Tab), 138.08 (s, CH in Tab), 133.67 (s, C-S of Tab), 124.03 (s, CH in IMe), 120.31 (s, CH in Tab), 56.35 (s, CH<sub>3</sub> in Tab), 37.75 (s, CH<sub>3</sub> in IMe).
- Preparation of [Pd<sub>4</sub>(IMe)<sub>4</sub>(Tab)<sub>6</sub>](OTf)<sub>6</sub>(Cl)<sub>2</sub> (5). Compound 5 was prepared as clear light yellow plate crystals in a manner similar to that described for 2, except that the amount of Tab was decreased to 0.15 mmol. Yield: 36 mg (52% based on Pd). Anal. Calcd. for C<sub>80</sub>H<sub>110</sub>N<sub>14</sub>O<sub>18</sub>F<sub>18</sub>S<sub>12</sub>Cl<sub>2</sub>Pd<sub>4</sub> (+5H<sub>2</sub>O): C 33.49, H 4.22,
- 70 N 6.83; found: C 33.53, H 4.85, N 7.44. IR (KBr disk): 3441 (s), 3108 (w), 3028 (w), 2949 (w), 2081 (w), 1632 (m), 1490 (s), 1404 (w), 1384 (m), 1346 (w), 1278 (m), 1225 (m), 1162 (m), 1124 (w), 1085 (w), 1063 (w), 1031 (s), 1009 (w), 958 (w), 938 (w), 848 (m), 747 (m), 717 (w), 672 (m), 640 (s), 576 (w), 558
- 75 (w), 518 (m) cm<sup>-1</sup>.<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, ppm):  $\delta$  8.74 (d, J = 8.8 Hz, 4H, CH in Tab), 8.08 (d, J = 8.8 Hz, 4H, CH in Tab), 7.75 (d, J = 8.9 Hz, 4H, CH in Tab), 7.58 (d, J = 8.9 Hz, 4H, CH in Tab), 7.35 (d, J = 9.0 Hz, 4H, CH in Tab), 7.20 (d, J = 8.9 Hz, 4H, CH in Tab), 6.74 (d, J = 4.7 Hz, 8H, CH in IMe), 3.77 (d, J =
- 80 8.0 Hz, 36H, CH<sub>3</sub> in Tab and IMe), 3.52 (s, 18H, CH<sub>3</sub> in Tab), 3.35 (s, 18H, CH<sub>3</sub> in Tab).<sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O, ppm):  $\delta$ 157.74 (s, C<sub>carbene</sub> in IMe), 145.91 (d, J = 19.3 Hz, C-N in Ph of Tab), 145.32 (s, C-N in Ph of Tab), 140.34 (s, C-N in Ph of Tab), 136.18 (d, J = 9.0 Hz, CH in Tab), 133.87-133.21 (m, C-S of
- <sup>85</sup> Tab), 132.68 (d, J = 28.6 Hz, C-S of Tab), 123.88 (d, J = 68.4 Hz, CH in IMe), 120.82 (s, CH in Tab), 119.92 (s, CH in Tab), 119.33 (s, CH in Tab), 57.21-55.88 (m, CH<sub>3</sub> in Tab), 37.44 (d, J= 6.0 Hz, CH<sub>3</sub> in IMe).

**Preparation of [Pd\_4Ag\_4(IMe)\_8(Tab)\_{10}](PF\_6)\_{12} (6).** The 90 synthetic route for 6 is the same as that for 4 2MeCN, except [Ag(IMe)<sub>2</sub>][AgCl<sub>2</sub>] (24 mg, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was used as additional Ag source. Yield: 38 mg (30% based on Ag). Anal. Calcd. for C130H194N26F72P12S10Ag4Pd4: C30.99, H 3.89, N 7.23; found: C 30.52, H 4.22, N 7.30. IR (KBr disk): 3442 (s), 95 2972 (w), 1629 (m), 1575 (w), 1490 (m), 1471 (w), 1441 (w), 1422 (w), 1385 (m), 1345 (w), 1313 (w), 1230 (m), 1201 (w), 1169 (w), 1125 (m), 1086 (w), 1011 (m), 959 (w), 938 (w), 843 (s), 748 (m), 717 (w), 685 (m), 665 (w), 558 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR

- (400 MHz, DMSO-d<sub>6</sub>, ppm): δ 7.67-7.29 (m, 40H, CH in Tab), 100 7.26 (s, 8H, CH in IMe), 6.94 (s, 8H, CH in IMe), 3.85 (s, 24H, CH<sub>3</sub> in IMe), 3.72 (s, 24H, CH<sub>3</sub> in IMe), 3.48 (d, J = 18.0 Hz, 90H, CH<sub>3</sub> in Tab). <sup>13</sup>C NMR (151 MHz, DMSO- $d_6$ , ppm):  $\delta$ 158.57 (s, C<sub>carbene</sub> in IMe), 145.41 (s, C-N in Ph of Tab), 138.07 (s, CH in Tab), 133.85 (d, J = 54.7 Hz, C-S of Tab), 124.03 (s, CH 105 in IMe), 123.38 (s, CH in IMe), 120.31 (s, CH in Tab), 119.07 (d,
- J = 37.1 Hz, CH in Tab), 56.40 (d, J = 15.6 Hz, CH<sub>3</sub> in Tab), 37.75 (s, CH<sub>3</sub> in IMe), 37.59 (s, CH<sub>3</sub> in IMe).

X-ray data collection and structural determination. Structure measurement of the six compounds were made on a 110 Bruker D8-Quest (2, 3a, 3b MeCN, 4 2 MeCN and 6) and an Agilent Xcalibur (5) CCD X-ray diffractometers by using graphite mono-chromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Each

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single crystal was mounted at the top of a glass fiber with grease in a stream of gaseous nitrogen. The cell parameter refinement and the data reduction were performed on the program Bruker D8 Quest for 2, 3a, 3b MeCN, 4 2MeCN, 6 and CrystAlisPro 5 (Agilent Technologies, Ver. 1.171.37.35, 2014) for 5, meanwhile an absorption correction (multi-scan method) was applied.<sup>11</sup> Direct methods and full-matrix least-squares techniques were used to solve and refine (on  $F^2$ ) all the crystal structures with SHELXTL-2013 program.<sup>12</sup> For **3a**, one of the IMe ligands, OTf 10 and Cl<sup>-</sup> displayed positional disorder with the relative ratios of 0.46/0.54, 0.62/0.38 and 0.68/0.32 refined for the two components. For 5, one-NMe<sub>3</sub> involving N5 displayed positional disorder with the relative ratios of 0.67/0.33 refined for the two components. One OTF was disordered with the relative ratios of 15 0.56/0.44 refined for the two components. The remaining Cl<sup>-</sup> was also disordered over four sites with occupancy factors for these components fixed at 0.40, 0.30, 0.20 and 0.10. For 6, one IMe displayed positional disorder with the relative ratios of 0.46/0.54refined for the two components. Two -NMe<sub>3</sub> groups displayed 20 rotational disorder with the relative ratios of 0.64/0.36 and 0.59/0.41 refined for the two components. One  $PF_6^-$  lies on a special position of higher symmetry than the molecule can possess. It is treated as spatial disorder by applying PART-1 and PART 0 in the .ins file with the site occupation factors changed to

- <sup>25</sup> 0.50 for its atoms. For **3a**, **5** and **6**, some spatially delocalized electron density (494 e for **3a**, 100 e for **5** and 117 e for **6**) in the lattices were found but acceptable refinement results could not be obtained for these electron densities. The solvent contributions were then modeled using SQUEEZE in the Platon program <sup>30</sup> suite.<sup>13</sup> As the NMR spectra for these compounds showed no obvious presence of solvents, these electron densities were therefore considered as water molecules. Thus the number of water molecules in these compounds are 49, 10 and 12, corresponding to **3a**  $\cdot$ 6H<sub>2</sub>O (Z = 8), **5**  $\cdot$ 10H<sub>2</sub>O (Z = 1) and **6**  $\cdot$ 3H<sub>2</sub>O <sup>35</sup> (Z = 4). The detailed crystallographic data and structure
- refinement parameters of **2**, **3a**, **3b** MeCN, **4** 2MeCN, **5** and **6** were summarized in Table 1.

**Catalytic study.** In a typical run, a mixture of aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2 mmol), <sup>40</sup> precatalyst and H<sub>2</sub>O (2 mL) were added into a 25 mL Schlenk tube. The mixture was stirred at 100 °C and cooled to ambient temperature after the desired reaction time. This is followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) for three times. The organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and removed in <sup>45</sup> *vacuo*. The crude product was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> and petroleum ether as eluents. The final pure product was dried in *vacuo* at 50°C for 12h.

Table 1 Crystal data and structure refinement parameters for 2, 3a, 3b·MeCN, 4·2MeCN, 5 and 6.

Compounds	2	3a	3b ⋅ MeCN	4·2MeCN	5	6
Empirical formul	a C <sub>30</sub> H <sub>42</sub> N <sub>6</sub> O <sub>6</sub> F <sub>6</sub> PdS <sub>4</sub>	$C_{29}H_{42}N_6O_3F_3ClPdS_3$	$C_{30}H_{45}N_7F_{12}P_2PdS_2$	$C_{42}H_{64}N_{12}F_{24}P_4Pd_2$	$S_2C_{80}H_{110}N_{14}O_{18}F_{18}Cl_2Pd_4S_{12}$	$_2 C_{130}H_{194}N_{26}F_{72}P_{12}Ag_4Pd_4S_{10}$
Formula weight	931.33	817.71	964.19	1593.85	2779.03	5038.42
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_{1}/c$	C2/c	$P2_1/n$	$P2_{1}/c$	<i>P</i> -1	C2/c
a/Å	16.4841(14)	30.6593(18)	15.2582(12)	10.4595(7)	12.6916(6)	39.487(9)
b/Å	10.5395(9)	8.5669(5)	8.1923(6)	12.4551(7)	15.6346(5)	18.813(4)
c/Å	11.6208(10)	33.864(2)	32.518(2)	25.8400(14)	17.4360(9)	29.645(6)
$\alpha$ /°	90	90	90	90	101.276(4)	90
$\beta/^{\circ}$	108.772(2)	102.117(2)	92.608(2)	112.347(3)	107.340(5)	115.292
γ/°	90	90	90	90	97.781(4)	90
$V/\text{\AA}^3$	1911.5(3)	8696.3(9)	4060.6(5)	3113.5(3)	3168.7(3)	19911(7)
$D_c/({\rm g~cm^{-3}})$	1.618	1.249	1.577	1.700	1.456	1.681
Ζ	2	8	4	2	1	4
$\mu$ (Mo–K $\alpha$ )/mm <sup>-1</sup>	0.783	0.677	0.726	0.862	0.882	1.056
<i>F</i> (000)	952	3360	1960	1600	1404	10064
Total reflections	33954	109630	78699	75783	32182	233883
Unique reflection	s 4395	9951	9329	7129	13957	24655
No observations	4051	8596	7571	6624	6175	14991
No parameters	246	534	498	396	739	1231
R <sub>int</sub>	0.0264	0.0446	0.0542	0.0433	0.0948	0.0961
$R^{a}$	0.0206	0.0692	0.0446	0.0361	0.0948	0.0607
$wR^b$	0.0524	0.1815	0.0941	0.0806	0.2270	0.1389
$GOF^{c}$	1.075	1.183	1.027	1.087	0.985	1.067

50  ${}^{a}R_{1} = ||F_{o}| - |F_{c}||/|F_{o}|$ .  ${}^{b}wR_{2} = [w(F_{o}^{2} - F_{c}^{2})^{2}/w(F_{o}^{2})^{2}]^{1/2}$ .  ${}^{c}GOF = \{w((F_{o}^{2} - F_{c}^{2})^{2})/(n-p)]\}^{1/2}$ , where n = number of reflections and p = total numbers of parameters refined.

#### **Results and discussion**

Synthetic and spectral aspects. As depicted in Scheme 1, treating the precursor compound 1 with three equiv. of Tab in the presence of two equiv. of AgOTf as the Cl<sup>-</sup> scavenger resulted in <sup>5</sup> the formation of *trans*-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)<sub>2</sub> (2) as yellow block crystals in 11% yield, accompanied by a few colourless block crystals of *cis*-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](OTf)(Cl) (3a). Alternating the Tab source as TabHPF<sub>6</sub> in the absence of AgOTf afforded a dinuclear compound [Pd<sub>2</sub>(IMe)<sub>4</sub>(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>·2MeCN <sup>10</sup> (4·2MeCN) in 35% yield, with the co-existence of trace amount of *cis*-[Pd(IMe)<sub>2</sub>(Tab)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·MeCN (3b·MeCN). In addition, a tetranuclear homometallic cluster [Pd<sub>4</sub>(IMe)<sub>4</sub>(Tab)<sub>6</sub>](OTf)<sub>6</sub>(Cl)<sub>2</sub>

1/1.5equiv. Tab/2 equiv. AgOTf. Finally, when we reacted 1 with 15 3 equiv. of TabHPF<sub>6</sub> and additional 0.5 equiv. of [Ag(IMe)<sub>2</sub>][AgCl<sub>2</sub>],<sup>14</sup> we are able to isolate an octanuclear heterometallic cluster of [Pd<sub>4</sub>Ag<sub>4</sub>(IMe)<sub>8</sub>(Tab)<sub>10</sub>](PF<sub>6</sub>)<sub>12</sub> (**6**, 30% yield) as the only product. We assume that for the formation of 2, the sequestration of the *trans*-located Cl<sup>-</sup> from 1 by Ag<sup>+</sup> is likely <sup>20</sup> the driving force to promote Tab association with the Pd center. The formation of 3a, 3b and 4 follows a multiple reaction sequence wherein *trans* effect<sup>15</sup> among IMe, Cl and Tab (IMe >Cl > Tab) and the reaction equilibrium dominate (Scheme S1). While the formation of **5** and **6** are collectively imposed by the <sup>25</sup> subtle interplay of Cl<sup>-</sup> precipitation, *trans* effect, as well as the coordination flexibility of Tab (**5** and **6**) and Ag(I) ion (**6**).



- <sup>30</sup> Compounds 2–6 are stable under aerobic conditions. Compounds 2, 3a and 5 are soluble in H<sub>2</sub>O, MeOH, EtOH, DMF and DMSO while 3b, 4 and 6 are soluble in MeCN, DMF and DMSO. The elemental analyses of the principal products 2, 4, 5 and 6 are in good agreement with their chemical formulae. In the <sup>35</sup> IR spectra of 2–6, bands at around 2950 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> are ascribed as methyl C-H stretching vibrations and C=C absorption in Tab or IMe. Bands around 1600 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, 1450 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> are typical skeletal vibrations of aromatic rings. Bands of C-N stretching vibrations and C-S weak absorption are <sup>40</sup> approximately at 1225 cm<sup>-1</sup> and 1005 cm<sup>-1</sup> in Tab. The S-O asymmetric stretching vibrations as well as C-F stretching vibrations for common OTf<sup>-</sup> anion in 2 and 5 are observed at about 1163 cm<sup>-1</sup> and 1030 cm<sup>-1</sup>. As for 4 and 6, bands at 843
- cm<sup>-1</sup> and 558 cm<sup>-1</sup> are ascribed to the P-F characteristic <sup>45</sup> stretching vibrations of their common anion PF<sub>6</sub><sup>-</sup>. Compounds 2– **6** are also characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra (ESI<sup>†</sup>). In the <sup>13</sup>C NMR spectra of **2**, **4**, **5** and **6**, the characteristic C<sub>IMe</sub>

singlets were found at 175.08 (2), 158.57 (4), 157.74 (5) and 158.57 (6) ppm. The relative downfield shift of 2 is due to its  $_{50}$  trans configuration.<sup>16</sup>

To further study the solution behaviours of **2**, **4**, **5** and **6**, we collected their ESI-MS data under positive mode in MeOH (**2** and **5**) or MeCN (**4** and **6**) solutions. The cationic fragments of **2** and **4** were identified as  $[Pd(IMe)_2(Tab)_2(OTf)]^+$  (m/z = 781.13, Fig. so S1a, ESI†) and  $[Pd_2(IMe)_4(Tab)_2(PF_6)]^{3+}$  (m/z = 359.07, Fig. S2a, ESI†). In addition, other cationic species, such as  $[Pd(IMe)(Tab)_2(OH) \cdot Et_2O \cdot MeOH \cdot H_2O]^+$ ,

 $[Pd(IMe)_{2}(Tab)(OH) \cdot 3MeOH]^{+} \text{ at } m/z = 677.18, 578.07 (2, Figs. S1b and S1c, ESI^{+}) and [Pd_{2}(IMe)_{3}(Tab)_{2}(PF_{6})_{3}]^{+},$ 60 [Pd(IMe)\_{2}(Tab)\_{2}(PF\_{6})]^{+}, [Pd(IMe)(Tab)\_{2}]^{2+} and [Pd(IMe)(Tab)(PF\_{6}) \cdot 2MeOH]^{+} at m/z = 1271.06, 777.16, 268.06,578.10 (4, Figs. S2b-S2e, ESI^{+}) were also found. Such observations were however not made for **5** and **6** wherein only dissociated cationic fragments were found. For **5**, only two peaks 65 at m/z = 686.08 and 602.54 were found, corresponding to

 $[Pd_2(IMe)_2(Tab)_4(OTf)_2]^{2+}$  and  $[Pd_2(IMe)_2(Tab)_3(OTf)_2]^{2+}$  (5,

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Figs. S3a and S3b, ESI<sup>†</sup>). In the case of **6**, mononuclear fragments such as  $[Pd(IMe)_2(Tab)_2]^{2+}$ ,  $[Pd(IMe)(Tab) \cdot 3MeOH]^{2+}$  and  $[Pd(IMe)(Tab)(PF_6) \cdot 2MeOH]^+$  at m/z = 316.09, 232.56 and 578.10 (**6**, Figs. S4a-S4c, ESI<sup>†</sup>) were accordingly identified. <sup>5</sup> Further analysis of the solution upon the isolation of **5** and **6** also indicated additional presence of Pd-IMe, Pd-IMe-Tab and Ag-IMe adducts, such as  $[Pd(IMe)(Tab) \cdot 4MeOH \cdot 2H_2O]^{2+}$  (m/z = 266.57),  $[Ag(IMe)_2 \cdot MeOH \cdot 4H_2O]^+$  (m/z = 403.03) (after removal of single crystals of **5**, Figs. S3c–S3d, ESI<sup>†</sup>), and  $[Pd(IMe)(OH) \cdot 2MeOH]^+$  (m/z = 233.16),  $[Ag(IMe)_2 \cdot 2H_2O]^+$  (m/z = 335.16),  $[Ag(IMe) \cdot 2H_2O]^+$  (m/z = 239.23) (after removal of single crystals of **6**, Figs. S4d–S4f, ESI<sup>†</sup>).



**Fig. 1** X-ray structures of (a)  $trans-[Pd(IMe)_2(Tab)_2]^{2+}$  of **2**, (b)  $[Pd_2(IMe)_4(\mu-Tab)_2]^{4+}$  of **4**, (c)  $cis-[Pd(IMe)_2(Tab)_2]^{2+}$  of **3a**, and (d)  $cis-[Pd(IMe)_2(Tab)_2]^{2+}$  of **3b**. All the dissociated moieties and H atoms are omitted. Colour codes: Pd (purple),S (yellow), N (blue), C (black).

Crystal structures of 2-6. As shown in Fig. 1a, the central Pd in 2 adopts a square-planar coordination with the two IMe and two Tab both in trans configurations. The average Pd-CIMe distance of 2.0205 Å (Table S1, ESI<sup>†</sup>) falls into the normal range 25 and comparable with other Pd-NHC complexes, such as  $[Pd(IMePP)_2][PF_6]_2$ (IMePP = 1-methyl-2-(pyridin-2yl)imidazo[1,5-a]pyridin-4-ylium, 1.995(7) Å),<sup>17</sup> (μ-Cp)(μ- $Cl)Pd_2(IPr)_2$  (Cp = cyclopentadienyl, IPr = 1,3-bis(2,6diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene, 2.022(4)  $_{30}$  Å)<sup>18</sup> and [Pd(MIBIPhen)(Cl)(H<sub>3</sub>CCN)]PF<sub>6</sub> (MIBIPhen = (3,3'-(biphenyl-2,2'-diylbis(methylene))bis(1-methyl-1H-imidazol-3ium)bromide), 2.021(2) Å).<sup>19</sup> In addition, the average Pd-S distance (2.3266 Å) is also comparable with those of  $[Pd_2(PPh_3)_2(Tab)_2(\mu-Tab)_2][PF_6]_4$  (2.3212(15) Å),<sup>20</sup> [(phen)\_2K( $\mu$ -

- <sup>35</sup> phen)<sub>2</sub>K(phen)<sub>2</sub>][(4-HC<sub>6</sub>F<sub>4</sub>S)<sub>2</sub>Pd( $\mu$ -SC<sub>6</sub>F<sub>4</sub>H-4)<sub>2</sub>Pd(SC<sub>6</sub>F<sub>4</sub>H-4)<sub>2</sub>] (phen = 1,10-phenanthroline, 2.333(3) Å)<sup>21</sup> and *cis*-[Pd(dppm)(pymt)<sub>2</sub>] (dppm = bis(diphenylphosphino)methane, pymt = pyrimidine-2-thiolate, 2.3267(9) Å).<sup>22</sup> For **4**, the two IMe ligands on each Pd center are *cis*, imposing the two Tab ligands
- <sup>40</sup> to adopt a *cis-anti* configuration and bridge a pair of Pd(IMe)<sub>2</sub> units to give a dimer (Fig. 1b). The Pd-C<sub>IMe</sub> and Pd-μ-S distances are 2.024 Å and 2.3776 Å on average, slightly longer than those in **2** (Table S1). As for **3a** and **3b**, their structures are similar except that their Tab ligands rotate to different degrees with respect to the C S hand (Figs. 1a and 1d).
- <sup>45</sup> respect to the C-S bond (Figs. 1c and 1d).



**Fig. 2** (a) The X-ray structure of  $[Pd_4(IMe)_4(Tab)_6]^{8+}$  of **5**, and (b) The Pd-S framework of **5**. All the dissociated moieties and H atoms are omitted. See Fig. 1 for colour codes. Symmetry code for (b): A – x, –y, 1 – z.

As illustrated in Fig. 2a, the structure of 5 can be readily assumed as a pair of Pd dimers linked by a pair of Tab ligands. Within the dimeric sub-unit, the Pd···Pd separation of 3.1289(9) Å exists. This distance is longer than that reported for the <sup>60</sup> Pd(I)···Pd(I) complex of  $[Pd_2(CH_3CN)_6][SbF_6]_2$  (2.4871(5) Å),<sup>23</sup> but comparable with that in  $[Pd_2(C_4H_6)_2(PPh_3)_2][PF_6]_2$  (3.1852(6) Å).<sup>24</sup> Such a Pd…Pd separation is notably shorter than the sum of their van der Waals radii of 3.26 Å, indication of Pd-Pd interaction. Within these dimeric units, each Pd(II) center is  $_{65}$  associated by three  $\mu$ -S atoms from three Tab ligands and one C atom from IMe. The Pd- $\mu$ -S distances are in the range of 2.324(2) Å to 2.388(2) Å (av. 2.351 Å). The Pd-C<sub>IMe</sub> bond lengths narrowly range from 1.995(11) Å to 2.023(10) Å (av. 2.009 Å) (Table S1, ESI<sup>†</sup>). The Pd-S framework of 5 can be considered as <sup>70</sup> a [Pd<sub>4</sub>S<sub>4</sub>] parallelogram wherein the four corners are defined by four S atoms, with two additional S atoms projecting two opposite directions with respect to the [Pd<sub>4</sub>S<sub>4</sub>] plane (Fig. 2b). All the atoms within the [Pd<sub>4</sub>S<sub>4</sub>] plane are nearly coplanar, with the maximum deviation of 0.3084 Å (S3 and S3A) and the minimum 75 deviation of 0.1720 Å (S2 and S2A) from the plane. The two projecting S atoms are 1.4784 Å away from the plane. Within the [Pd<sub>4</sub>S<sub>4</sub>] plane, the four Pd atoms form a rectangle with size of  $3.734 \times 3.129 \text{ Å}^2$ .



**Fig. 3** (a) The X-ray structure of  $[Pd_4Ag_4(IMe)_8(Tab)_{10}]^{12+}$  of **6**, and (b) The Pd-Ag-S skeleton of **6**. All the dissociated moieties and hydrogen atoms are omitted. See Fig. 1 for colour codes except for Ag (cyan).

- <sup>10</sup> Compound **6** features an octanuclear [Pd<sub>4</sub>Ag<sub>4</sub>(IMe)<sub>8</sub>(Tab)<sub>10</sub>]<sup>12+</sup> dodeca-cation (Fig. 3a). The identities of Ag and Pd centers are distinguished by their coordination preferences (square planar for Pd and trigonal/tetrahedral for Ag), as well as the charge counting. The overall skeleton of **6** (Pd<sub>4</sub>Ag<sub>4</sub>S<sub>10</sub>, Fig. 3b) is oval-shaped with <sup>15</sup> an inversion center coinciding with the middle of the central Ag<sup>...</sup>Ag bond. By detaching two PdS<sub>2</sub> motifs at the polar positions, we can easily assume the remaining part (Pd<sub>2</sub>Ag<sub>4</sub>S<sub>6</sub>) as an edge-fused norbornane-like framework. The two parts bearing norbornane topology are fused through one of their overhead <sup>20</sup> bridges (Ag<sup>...</sup>Ag separation). The Ag<sup>...</sup>Ag separation of 3.0004(10) Å is significantly shorter than the sum of van der
- Waals radii of 3.44 Å, indicating strong Ag. Ag interaction. It is also notable that the Pd. Ag distance from the polar Pd atom to the closest Ag features 3.2482(9) Å, shorter than the sum of their up der Waals radii and a strong a strong stron
- <sup>25</sup> van der Waals radii of 3.35 Å, also an indication of strong Pd...Ag interaction. Each Pd atom adopts a square-planar geometry and is associated with two *cis*-located IMe ligands and two bridging Tab, in a *cis-syn* fashion and contrasting that found in the dimeric compound **4**. The polar Pd center extends to the
- <sup>30</sup> Ag center *via* a pair of  $\mu$ -Tab, while the other type of Pd extends to three Ag centers *via* one  $\mu$ -Tab and one  $\mu_3$ -Tab. The three Ag centers further cascade *via* one additional S and one Ag···Ag interaction. Each Ag atom in turn employs a distorted (pseudo) tetrahedron coordination mode. The Ag atoms associated with the
- <sup>35</sup> polar Pd atoms are bonded by three  $\mu$ -Tab and one  $\mu_3$ -Tab while the two central Ag atoms are coordinated by two  $\mu$ -Tab, one  $\mu_3$ -Tab and one Ag atom. The Pd- $\mu$ -S, Pd- $\mu_3$ -S and Pd-C<sub>IMe</sub> bond

lengths are 2.3786 Å, 2.3620 Å and 2.012 Å on average. The average Ag- $\mu$ -S and Ag- $\mu$ -S distances are 2.5443 Å and 2.6230 <sup>40</sup> Å (Table S1, ESI<sup>†</sup>).

 Table 2
 Suzuki-Miyaura coupling of aryl bromide with phenylboronic acid.

0. ``	Br	+	(OH) <sub>2</sub>	→∽		»
Entry <sup>a</sup>	Pre- catalyst	Base	Pd loading (mol%)	Т (°С)	Time (h)	Yield <sup>b</sup> (%)
1	5	Na <sub>2</sub> CO <sub>3</sub>	0.01	100	24	92
2	5	K <sub>2</sub> CO <sub>3</sub>	0.01	100	24	75
3	5	$K_3PO_4$	0.01	100	24	82
4	5	NaOAc	0.01	100	24	40
5	5	$Cs_2CO_3$	0.01	100	24	71
6	5	NaOH	0.01	100	24	95
7	5	KOH	0.01	100	24	99
8	5	KOH	0.005	100	24	99
9	5	KOH	0.001	100	24	99
10	5	KOH	0.0005	100	24	99
11	5	KOH	0.0004	100	24	96
12	5	KOH	0.0005	90	24	94
13	5	KOH	0.0005	100	6	80
14	5	KOH	0.005	100	6	88
15	5	KOH	0.01	100	6	99
16	5	KOH	0.01	100	4	91
17	2	Na <sub>2</sub> CO <sub>3</sub>	0.01	100	24	84

<sup>*a*</sup> Reaction conditions: 1 mmol of 4-bromoacetophenone, 1.5 mmol of phenylboronic acid, 2 mmol of base, 2.0 mL H<sub>2</sub>O, the reactions are carried out under N<sub>2</sub>. <sup>*b*</sup>Isolated yield.

To evaluate the suitability of Pd-NHC-Tab compounds as potential catalysts, we firstly selected water-soluble compound **5** <sup>45</sup> as the precatalyst for the Suzuki-Miyaura cross-coupling reaction in water. We chose coupling reaction between 4bromoacetophenone (1.0 mmol) and phenylboronic acid (1.5 mmol) as the model reaction. The base, Pd loading, reaction temperature and time were subsequently optimized. As shown in <sup>50</sup> Table 2, the optimal Pd loading is 0.0005 mol% with KOH as the base (Table 2, entry 10), while the yield expectedly decreased upon sequentially reducing the Pd loading (Table 2, entry 11).

It is apparent that the reaction temperature significantly impacts the reaction rate, with refluxing condition being optimal (100 °C). Using 0.0005 mol% Pd loading and 24 h as the reaction time, the yield decreased from 99% to 94% when temperature changed from 100 °C to 90 °C (Table 2, entries 10 and 12). Further reducing the time to 6 h (0.0005 mol% Pd loading, 100 °C) leads to drastic yield reduction to 80% (Table 2, entry 13). The yield decrease caused by time cut can be compensated by increasing the Pd loading. Thus, a high yield of 99% (Table 2, entry 15) can be achieved with 0.01 mol% Pd loading at 100 °C for 6 h. Since compound **2** is also soluble in H<sub>2</sub>O, its catalytic activity is examined under the identical conditions (Na<sub>2</sub>CO<sub>3</sub>, 0.01 cs mol% Pd loading, 100 °C, 24 h). It turns out that **2** is less effective than **5** and the yield decreased from 92% to 84% (Table 2, entry 17). The investigation of the catalytic property of other

compounds is either hindered by the low yield of the catalysts (**3a** and **3b**) or the solubility of the catalysts (**4** and **6**) in water.

Table 3	Suzuki-Miyaura	coupling	of aryl	bromide	with	phenylboronic
5 acid.						

Entry <sup>a</sup> Ar-Br         Yield <sup>b</sup> (%)           1         4-bromoacetophenone         99           2         4-bromobenzonitrile         83           3         4-bromobenzaldehyde         90           4         4-bromonitrobenzene         96           5         4-bromofluorobenzene         41 $6^c$ $\beta$ -bromonaphthalene         89 $7^c$ 4-bromotoluene         51 $8^d$ 4-bromotoluene         49	R Br	+	
14-bromoacetophenone9924-bromobenzonitrile8334-bromobenzaldehyde9044-bromonitrobenzene9654-bromofluorobenzene41 $6^c$ $\beta$ -bromonaphthalene89 $7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	Entry <sup>a</sup>	Ar-Br	Yield <sup>b</sup> (%)
24-bromobenzonitrile8334-bromobenzaldehyde9044-bromonitrobenzene9654-bromofluorobenzene41 $6^c$ $\beta$ -bromonaphthalene89 $7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	1	4-bromoacetophenone	99
34-bromobenzaldehyde9044-bromonitrobenzene9654-bromofluorobenzene41 $6^c$ $\beta$ -bromonaphthalene89 $7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	2	4-bromobenzonitrile	83
44-bromonitrobenzene9654-bromofluorobenzene41 $6^c$ $\beta$ -bromonaphthalene89 $7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	3	4-bromobenzaldehyde	90
54-bromofluorobenzene41 $6^c$ $\beta$ -bromonaphthalene89 $7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	4	4-bromonitrobenzene	96
$6^c$ β-bromonaphthalene89 $7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	5	4-bromofluorobenzene	41
$7^c$ 4-bromoanisole51 $8^d$ 4-bromotoluene49	6 <sup><i>c</i></sup>	$\beta$ -bromonaphthalene	89
8 <sup><i>d</i></sup> 4-bromotoluene 49	$7^c$	4-bromoanisole	51
	$8^d$	4-bromotoluene	49
9 <sup><i>d</i></sup> bromobenzene 54	$9^d$	bromobenzene	54

<sup>*a*</sup> Reaction conditions: 1.0 mmol of aryl bromide, 1.5 mmol of phenylboronicacid, 2.0 mmol base, 2.0 mL H<sub>2</sub>O, 0.01 mol% Pd loading, 6h, 100°C under nitrogen.<sup>*b*</sup> Isolated yield.<sup>*c*</sup>0.05 mol% Pd loading. <sup>*d*</sup>0.1 mol% Pd loading.

After acquiring the optimized reaction conditions, we expanded the substrate scope from electron-poor aryl bromides to electron-rich ones. From Table 3, it can be concluded that bromide substrates bearing electron-withdrawing substituents <sup>15</sup> such as -COCH<sub>3</sub>, -CN, -CHO, -NO<sub>2</sub> and -F are advantageous for the reaction (Table 3, entries 1–5).<sup>25</sup> Accordingly, the -F group with the weakest electron-withdrawing ability results in the lowest yield (Table 3, entry 5). Including electron-donating groups like -OCH<sub>3</sub> and -CH<sub>3</sub> or-H in the bromide substrates are <sup>20</sup> un-favoured (Table 3, entries 7–9). When the aryl changes from phenyl to naphthyl, the yield also drops dramatically (Table 3, entry 6). Our further analysis of the ESI-MS upon completion of the catalysis (with **5** as the precatalyst) revealed that two additional peaks at m/z = 387.06 and 427.04 exist, corresponding

<sup>25</sup> to two cationic species  $[Pd(IMe)(CI) \cdot 3MeOH \cdot 3H_2O]^+$  and  $[Pd(IMe)(OH) \cdot 2MeOH \cdot 8H_2O]^+$ , respectively. This observation suggests that during the catalysis, the Pd-C bond remains robust and the precatalyst undergoes a Pd-S bond dissociation to enter the catalytic cycle.

#### **30 Conclusions**

In this paper, the reactivity of NHC-ligated Pd compound 1 as the precursor towards Tab has been explored with interesting structural outcome. Compounds 2–6 isolated herein range from mononuclear to octanuclear, revealing the bridging flexibility of

- <sup>35</sup> the Tab ligand. The relative positions of NHC and Tab can be readily switched from *cis* to *trans* depending on the reaction parameters. In addition, the circumduction and rotation of the -PhNMe<sub>3</sub> moiety in Tab with respect to the C-S bond render much flexibility of the system and facilitate the molecular packing.
- <sup>40</sup> Notably, additional heteroatom (Ag) can be easily included in the structural framework to give a Pd-Ag heterometallic octanuclear cluster of **6**, highlighting the broad potential of such system in hosting other useful heterometallic metals such as Ru, Ir and Au,

to achieve functional molecular assemblies with heterometallic 45 synergy in catalysis. Our preliminary experiments demonstrated that **5** showed excellent catalytic activity(a very low Pd loading of 0.0005 mol%) towards Suzuki-Miyaura coupling of phenylboronic acid with 4-bromoacetophenone in water. In view of the fascinating development in carbene chemistry, and their <sup>50</sup> interaction with diverse transition and main group metal ions, as well as their potential in broad areas, our future work is to extend the scope of both NHC and homo-/hetero-metal ions and to unveil their structural complexity and their applications in catalysis.

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\*Electronic Supplementary Information (ESI) available: Detailed ESI-MS and NMR data for compounds **2**, **4**, **5** and **6**, the catalytic data. CCDC 1505255–1505260 for compounds **2–6**. For ESI and crystallographic data 75 in CIF or other electronic format see DOI:10.1039/b000000x/

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#### **Contents for Graphical Abstract**

Combination of Pd(II), an N-heterocyclic carbene (NHC), and a thiolate (Tab) yields several Pd-NHC-Tab complexes and an octanuclear Pd<sub>4</sub>Ag<sub>4</sub>-NHC-Tab cluster.

#### **Figure for Graphical Abstract**

