

# Reactivity towards Nitriles, Cyanamides, and Carbodiimides of Palladium Complexes Derived from Benzyl Alcohol. Synthesis of a Mixed Pd<sub>2</sub>Ag Complex.

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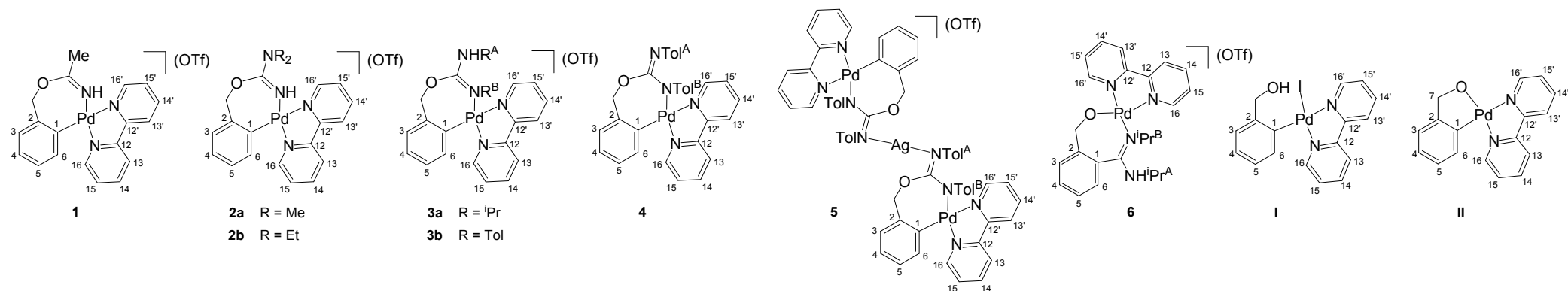
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**Table S.1.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR Data ( $\text{CDCl}_3$ , r.t. (except  $^{13}\text{C}$  data for **4**)) of Complexes **1-6**, **I**,<sup>1</sup> and **II**.<sup>1,(a)</sup>

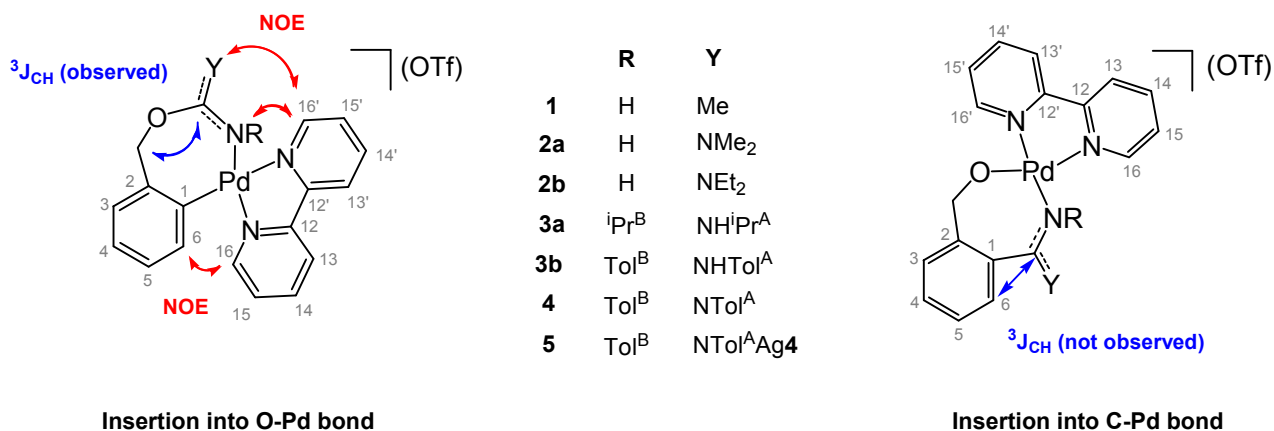


Aryl ligand	<b>1</b>		<b>2a</b> (R=Me)		<b>2b</b> (R=Et)		<b>3b</b> (R=Tol)		<b>4</b>		<b>5</b>		<b>3a</b> (R= $i$ Pr)		<b>6</b>		<b>I</b>		<b>II</b>																						
	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}^{(b)}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$	$^{13}\text{C}$	$^1\text{H}$																					
<b>C1</b>	152.0		153.1		153.0		153.7		149.6		150.0		153.6		<b>134.2</b>		146.3		151.0																						
<b>C2</b>	139.4		139.3		139.1		137.9		140.7		138.9		138.3		<b>146.0</b>		145.4		<b>166.2</b>																						
<b>CH3</b>	127.6	7.15-	127.6	7.16-	127.4	7.14-	127.9	7.22-	124.9	6.70	126.6	6.66	127.4	7.03	130.8	7.43	128.8	7.11	119.1																						
<b>CH4</b>	125.4	7.11	125.1	7.10	125.0	7.12	125.6	7.18	123.5	6.93	124.1	7.17	124.7	7.07	131.3	7.40	124.3	6.93-	124.0	7.04-																					
<b>CH5</b>	130.6	7.29	130.3	7.29-	130.2	7.29-	131.2	7.44	126.9	7.03	127.2	7.36	129.8	7.26	127.9	7.32	126.8	6.89	123.6	6.97																					
<b>CH6</b>	134.7	7.22	134.9	7.26	134.9	7.26	134.2	7.50	136.2	7.70	136.1	7.84	134.4	7.39	128.0	7.55	136.6	7.38	131.7	7.21																					
<b>CH<sub>2</sub></b>	72.2	6.60 5.05	73.2	6.62 5.10	73.1	6.66 5.11	74.2	7.22 5.27	71.2	5.02 4.73 (br)	72.9	4.88 4.19	74.3	6.65 5.12	69.9	4.57 3.84	68.7	4.99 4.48	<b>78.4</b>	<b>5.21</b>																					
<b>C=NH/ NH</b>	175.1	<b>8.45</b>	161.3	4.81	160.2	4.76	156.5	6.49	155.7		162.2		156.3	5.57	162.0	6.39																									
<b>Bpy<sup>(f)</sup></b>																																									
																						<b>Tol<sup>A</sup></b>	<i>i</i> -C	133.4		147.9		143.6			143.6			45.4	3.89	48.9	3.55			<b>CH<sup>A</sup></b>	<b><math>i</math>Pr<sup>A</sup></b>
																							<i>o</i> -CH	123.9	6.85	122.7	7.00-6.95	(e)	<b>6.85 (br)</b>				23.7	1.28	25.2	1.04			<b>Me<sup>A</sup> (e)</b>		
																							<i>m</i> -CH	129.9	7.09	129.0	(br)	<b>129.7 (br)</b>	(e)				23.1	1.14	23.1	1.40					
																						<b>Tol<sup>B</sup></b>	<i>i</i> -C	141.8		146.4		146.4			146.4			51.0	3.78	50.7	4.25			<b>CH<sup>B</sup></b>	<b><math>i</math>Pr<sup>B</sup></b>
																							<i>o</i> -CH	125.9	7.29	124.6	7.9 (d)	124.2	6.13				26.0	1.55	24.9	1.65			<b>Me<sup>B</sup> (e)</b>		
<i>m</i> -CH	131.3	7.20	128.9	6.85	128.7	7.00				22.0	0.70	22.4	1.54																												
<b>C12</b>	157.0		157.0		157.0		156.9		155.2		156.5		156.9		154.8		156.6		156.6																						
<b>C12'</b>	152.6		153.1		153.2		153.4		153.1		153.7		153.1		155.7		154.4		153.4																						
<b>CH16</b>	151.9	8.37	151.6	8.32	151.6	8.32	151.6	8.31	152.1	8.45	152.4	8.35	151.7	8.52	152.2	8.52	<b>150.4</b>	<b>7.33</b>	152.0	9.18																					
<b>CH16'</b>	151.0	8.89	149.1	8.65	148.9	8.58	149.3	8.61	149.3	8.39	149.0	8.13	150.8	8.68	148.1	8.85	<b>153.1</b>	9.46	149.9	9.03																					
<b>CH14</b>	140.1	8.07	140.3	8.14	140.3	8.15	141.0	8.18	138.8	7.96	139.8	8.10	140.3	8.16	140.1	8.00	139.6	7.94	138.1	8.03-																					
<b>CH14'</b>	140.1	8.11	140.5	8.08	140.6	8.13		8.14	139.1	7.91	139.9	8.00	140.4	8.15	140.6	8.08	139.5	7.98	138.8	7.96																					
<b>CH15</b>	126.7	7.43	126.7	7.39	126.7	7.39	126.9	7.39	126.7	7.39	126.8	7.36	126.9	7.44	128.4	7.71	127.2	7.25	126.6	7.59-																					
<b>CH15'</b>	128.3	7.82	127.9	7.79	127.7	7.78	127.5	7.69	127.0	-7.30	126.9	7.31	128.2	7.82	126.1	7.55	127.6	7.53	126.3	7.52																					
<b>CH13</b>	123.0	8.25	123.8	8.42	123.9	8.44	124.5	8.54	122.1	8.06	123.4	8.33	123.5	8.40	122.8	8.04	122.8	8.06-	122.5	8.08-																					
<b>CH13'</b>	122.1	8.17	123.0	8.35	123.2	8.39	123.8	8.50	121.6	8.02	122.7	8.28	122.7	8.35	122.4	8.08	122.4	8.02	121.1	8.03																					

(a) The data for the Me groups of **1**, **2a**, **3b**, **4**, **5** and the Et groups of **2b** are not included in the tables for lack of space and relevance. The data highlighted in bold are commented in the next section. (b) Measured at 213K. (c) The Tol<sup>A</sup> group in **5** is fluxional: for the *o*-CH the <sup>13</sup>C resonance is not observed and the <sup>1</sup>H resonance is broad; for the *m*-CH the <sup>13</sup>C resonance is broad and the <sup>1</sup>H resonance is not observed. (d) This resonance appears in a multiplet together with the resonances of H13,13',14,14'. (e) For each Me group the corresponding <sup>13</sup>C and <sup>1</sup>H resonances are in the same line. (f) The two halves of the tbbpy and bpy ligands have been assigned based on NOE contacts between H16 and the aryl group.

## Extended Comments on the NMR Data

For the complexes **1-5** the insertion of the organic molecules ( $\text{MeC}\equiv\text{N}$ ,  $\text{R}_2\text{NC}\equiv\text{N}$ , or  $\text{RN}=\text{C}=\text{NR}$ ) into the O-Pd bond, and not the C-Pd bond, is confirmed by the  $^1\text{H},^{13}\text{C}$ -HMBC spectrum, where the 3-bond correlation between the inserted C=N carbon and the methylenic  $\text{CH}_2\text{O}$  protons is always observed, while no correlation is observed between the C=N carbon and the aryl H6 proton, as would be the case for an insertion into the C-Pd bond (Scheme S.1). The halves of the bpy ligand in these complexes have been assigned based on NOE contacts between H16 and H6 of the aryl group and between H16' and the protons which are close in space (see also Scheme S.1).



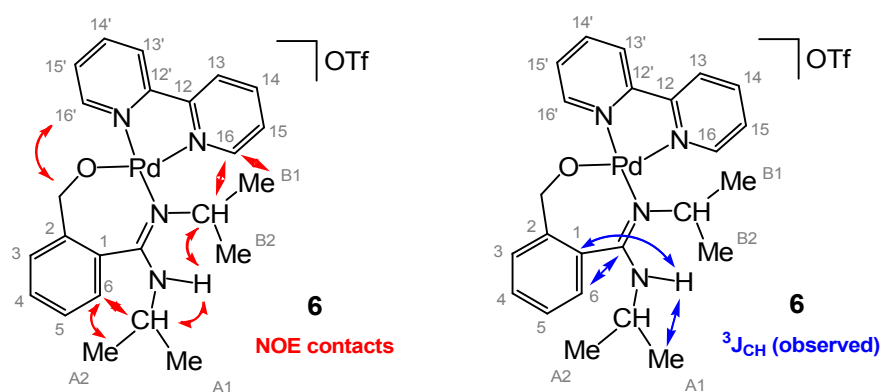
Insertion into O-Pd bond

Insertion into C-Pd bond

**Scheme S.1.** In blue: expected  $^3\text{J}(^{13}\text{C}-^1\text{H})$  correlations in the complexes resulting from the insertion of the organic molecules ( $\text{MeC}\equiv\text{N}$ ,  $\text{R}_2\text{N}-\text{C}\equiv\text{N}$ , or  $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$ ) into the O-Pd bond (left) or C-Pd bond (right) of **II**. Only the  $^3\text{J}_{\text{CH}}$  coupling between the C=N carbon and the methylenic protons is observed, indicating insertion into the O-Pd bond. In red: assignment of the halves of the bpy ligand in **1-5**, based on selective NOE contacts.

In complex **6**, the insertion of the carbodiimide into the C-Pd bond is confirmed by the  $^1\text{H},^{13}\text{C}$ -HMBC and  $^1\text{H}$ -NOESY experiments (Scheme S.2). The halves of the bpy ligand are assigned based on the NOE contacts, as well. Complex **6** is not an aryl palladium complex and this is reflected in the

chemical shifts of the aryl carbons, which differ from those of **1-5**, especially for C1 ( $\delta$  134 ppm for **6** and 149.6-153.7 ppm for **1-5**) and C2 ( $\delta$  146 ppm for **6** and 137.9-140.7 ppm for **1-5**).



**Scheme S.2.** Observed NOE contacts between different groups in complex **6** (left), and observed  $^3J(^{13}\text{C}, ^1\text{H})$  correlations in the  $^1\text{H}, ^{13}\text{C}$ -HMBC spectrum (right), both confirming the insertion of the carbodiimide into the C-Pd bond, as well as the position of the proton on the uncoordinated nitrogen.

The two  $^i\text{Pr}$  groups in **3a** and **6**, as well as the two Tol groups in **3b**, **4**, and **5**, are assigned based on NOE data. The two Me groups within each  $^i\text{Pr}$  are always diastereotopic (inequivalent), as are the methylenic protons of all the complexes (**1-6**). The methinic proton of  $^i\text{Pr}^A$  resonates as a doublet of septets ( $^3J_{\text{HH}} = 7$  Hz,  $^3J_{\text{HH}} = 6$  Hz for **3a**, and  $^3J_{\text{HH}} = 9$  Hz,  $^3J_{\text{HH}} = 6$  Hz for **6**), because of the coupling with the six methyl protons and the NH proton, which appears as a doublet ( $^3J_{\text{HH}} = 7$  Hz for **3a**, and  $^3J_{\text{HH}} = 9$  Hz for **6**). This coupling pattern confirms the position of the NH proton in **3a** and **6** on the N that is not coordinated to Pd, as revealed by the X-ray data of **3a**. This position is similar to that observed in the related complexes resulting from the reaction with carbodiimides of complexes derived from benzyl alcohol.<sup>2,3</sup> The  $^1\text{H}$ -NOESY and  $^1\text{H}, ^{13}\text{C}$ -HMBC spectra of **3a,b** and **6** (see Scheme S.2 for **6**) also confirm the position of the proton on the uncoordinated nitrogen.

The C=NH proton in complex **1** resonates at much higher frequency ( $\delta$  8.45 ppm) than in **2a,b** ( $\delta$  4.81 and 4.76 ppm), for which the partial release of the lone pair from the  $\text{NR}_2$  group results in resonance form with a negative charge on the NH, an effect that is lacking in **1**. This electronic

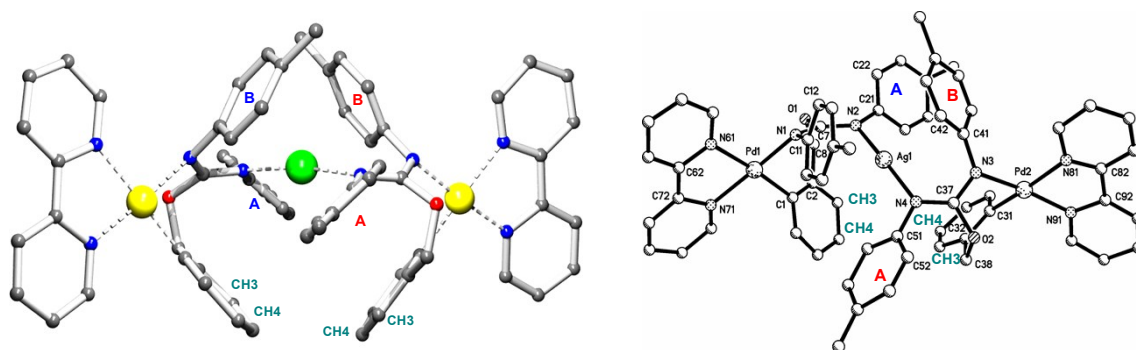
delocalization along the R<sub>2</sub>N-C=NH bonds is confirmed by the X-ray diffraction study of **2a** (see the X-ray Structure Determinations section in the Article). For the complexes derived from carbodiimides, the three NHR chemical shifts are similar:  $\delta$  5.57 ppm for **3a**, 6.49 ppm for **3b** and 6.39 ppm for **6**.

The neutral complex **4** shows a fluxional behaviour within the chelate ring, with a broadening in one of the methylenic <sup>1</sup>H resonances and in the <sup>1</sup>H resonances of the Tol<sup>A</sup>. This broadening disappears at low temperature (213 K), but the <sup>1</sup>H chemical shifts do not change significantly, so that the values at room temperature are given in Table S.1 and in the Experimental Section of the Article. In the APT spectrum at room temperature, however, the S/N ratio is low and many resonances are missing, so that the <sup>13</sup>C NMR data at 213 K are given.

In the trinuclear Pd<sub>2</sub>Ag complex **5** the halves of the molecule are equivalent in solution, and only one set of <sup>1</sup>H and <sup>13</sup>C NMR resonances is observed. This is in contrast to what we have recently observed for another “dimeric” complex, [C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>OCH<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>{PdBr(bpy)}-2)}<sub>2</sub>-1,4], where the halves of the molecule were not equivalent.<sup>1</sup> The chelate nature of the Pd moieties in **5**, as well as the linear geometry of the Ag bridge, seem to favor the symmetry of this complex in solution. The Tol<sup>A</sup> group in **5** shows strongly broadened <sup>1</sup>H and <sup>13</sup>C resonances, indicating that the rotation around the Tol-N bond is hindered by the steric crowding in the molecule. Curiously, in the <sup>1</sup>H spectrum the resonance of the *o*-CH<sup>A</sup> group is very broad and the resonance of the *m*-CH<sup>A</sup> group is not observed, while in the <sup>13</sup>C spectrum the opposite is observed: *m*-CH<sup>A</sup> broad and *o*-CH<sup>A</sup> not observed.<sup>1</sup> This different behaviour in the <sup>1</sup>H and <sup>13</sup>C spectra can be explained by the frequency dependence of the NMR timescale. The Tol groups A and B are distinguished because Tol<sup>A</sup> shows NOE contacts with H<sub>3,4</sub> of the aryl group, as expected from the X-ray structure (Figure S.1).

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<sup>1</sup> This resonances have been assigned based on <sup>1</sup>H,<sup>13</sup>C correlation and <sup>1</sup>H NOE data. The chemical shifts are also similar to those of the related complex **4**.

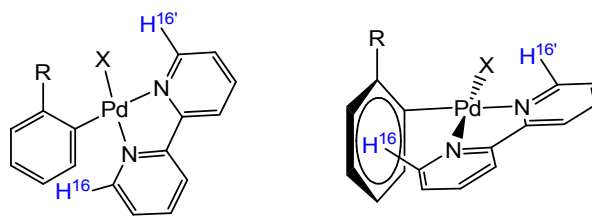


**Figure S.1.** X-ray structure of **5**, showing the proximity in space of the *o*-H of Tol<sup>A</sup> with the protons H3,4 of the aryl group.

Within the bpy ligand, we observe that for the aryl palladium complexes **1-5**,  $\delta(\text{C12}) > \delta(\text{C12}')$  (for C12, in the pyridyl ring *trans* to N,  $\delta = 157.0\text{-}155.2$  ppm, while for C12', in the pyridyl ring *trans* to aryl,  $\delta = 153.7\text{-}152.6$  ppm). We had already observed in a previous paper, including complexes **I** and **II**,<sup>1</sup> that  $\delta(\text{C12})$  (*trans* to I, Br, O, 156.6-155.2 ppm)  $>$   $\delta(\text{C12}')$  (*trans* to aryl, 154.5-153.4 ppm). Combining now all the data it is clear that  $\delta(\text{C12})$  (*trans* to I, Br, O, N, 157.0-155.2 ppm) is always larger than  $\delta(\text{C12}')$  (*trans* to aryl, 154.5-152.6 ppm). For complex **6**, the C12,12' chemical shifts are:  $\delta(\text{C12}) = 154.8$  ppm (*trans* to O);  $\delta(\text{C12}') = 155.7$  ppm (*trans* to N).

For **1-6**,  $\delta(\text{CH16})$  (152.4-151.6 ppm) is also larger than  $\delta(\text{CH16}')$  (151.0-148.1 ppm), although the difference is smaller than for C12,12'. In the iodo complex **I** however, this tendency is reversed ( $\delta(\text{CH16})$ , 150.4 ppm  $<$   $\delta(\text{CH16}')$ , 153.1 ppm), as we had already noted in our previous paper.<sup>1</sup>

The chemical shifts of the *ortho* hydrogen atoms of both pyridyl rings, H16 and H16', are rather similar for **1-5** (H16,  $\delta$  8.31-8.52 ppm; H16',  $\delta$  8.13-8.89 ppm). Usually, in aryl-Pd complexes the protons H16 (in the ring *cis* to the aryl group) are strongly shielded with respect to H16', as a consequence of the anisotropic effect of the aryl group (Scheme S.3).<sup>1,4,5</sup> Thus, for **I**,  $\delta(\text{H16}) = 7.33$  ppm and  $\delta(\text{H16}') = 9.46$  ppm. The chelate nature of complexes **1-5**, which forces the orientation of the aryl ring towards the plane of the bpy ligand, would explain the absence of this effect (similarly to what is observed for the cyclized complex **II**,<sup>1</sup> where  $\delta(\text{H16}) = 9.18$  ppm and  $\delta(\text{H16}') = 9.03$  ppm).

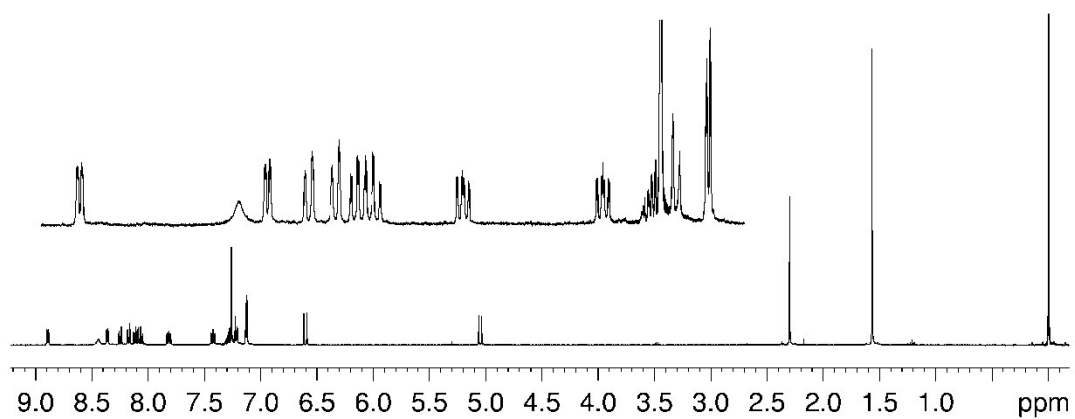
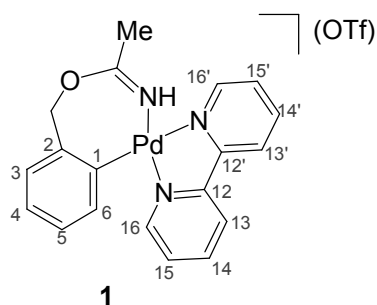


**Scheme S.3.** Anisotropic effect of the aryl ligand on the H16 protons of a bpy ligand. The *ortho* substituent (R) usually hinders the rotation around the Ar-Pd bond. However, even when this rotation is allowed, e.g. in the complex [PdXPh(bpy)] (X = Br, I),<sup>6</sup> the Ar group still adopts a perpendicular orientation with respect to the [PdX(N^N)] plane and the shielding of the H16 proton is observed

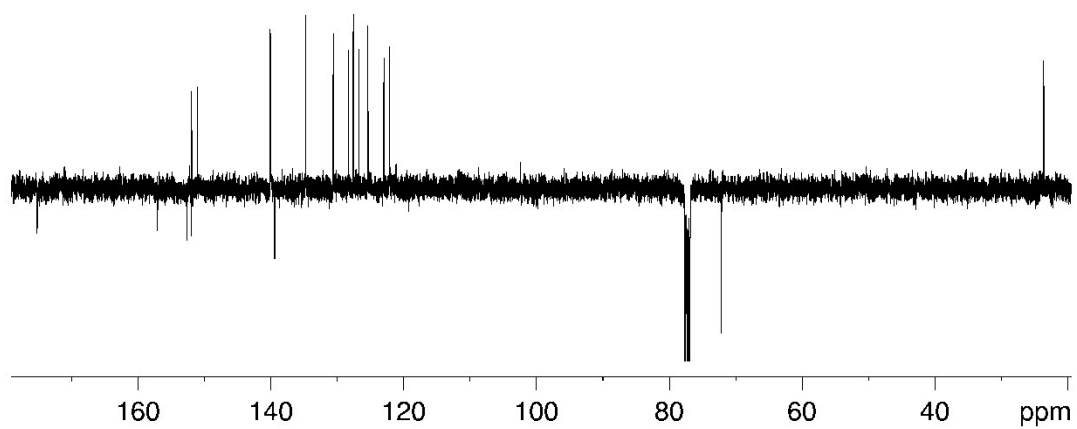


## NMR Spectra of Complexes 1-6

[Pd{ $\kappa^2$ -C,N-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>OC(=NH)Me}-2}(bpy)](OTf) (**1**)

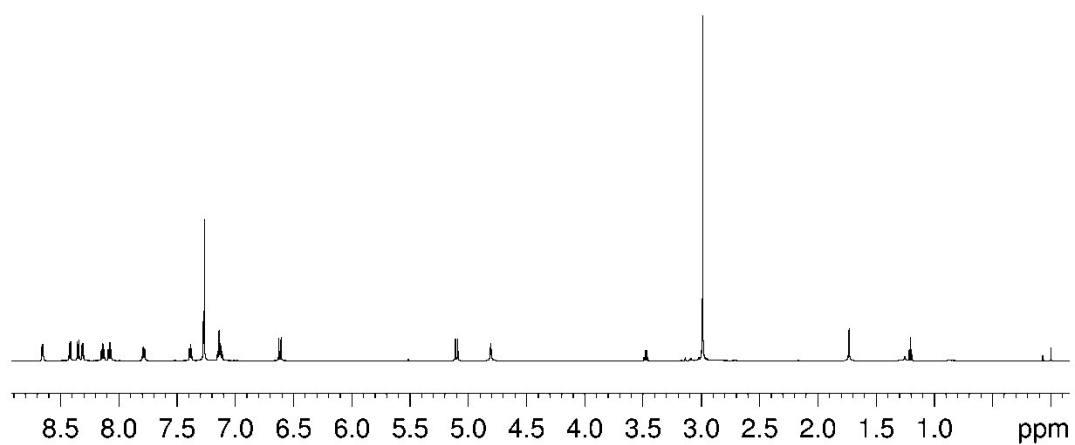
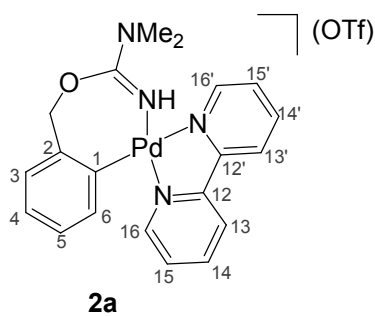


<sup>1</sup>H-RMN spectrum (400 MHz) of **1**

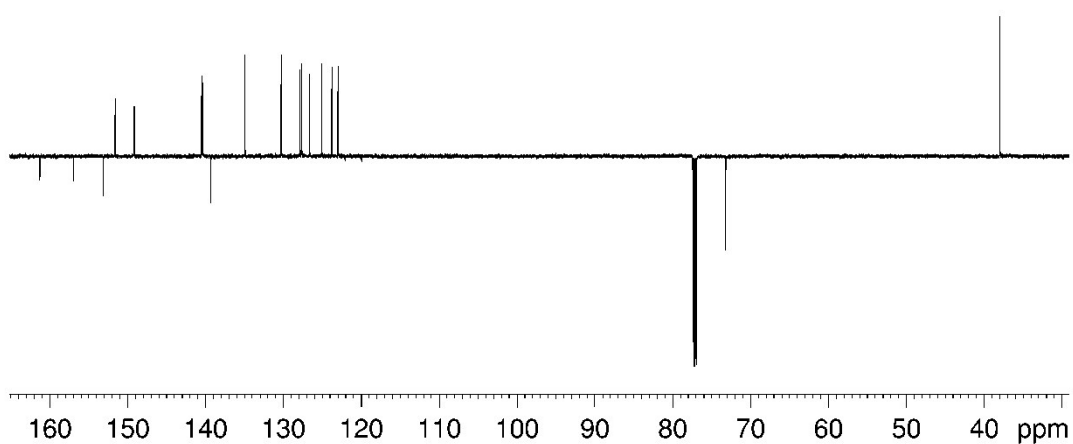


APT spectrum (100.6 MHz) of **1**

$[\text{Pd}\{\kappa^2\text{-C},\text{N-C}_6\text{H}_4\{\text{CH}_2\text{OC(=NH)NMe}_2\}\text{-2}\}\{\text{bpy}\}](\text{OTf})$  (**2a**)

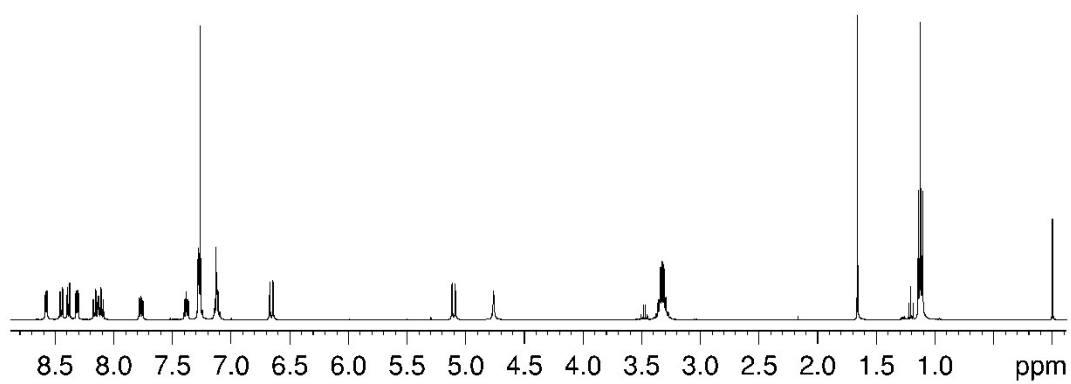
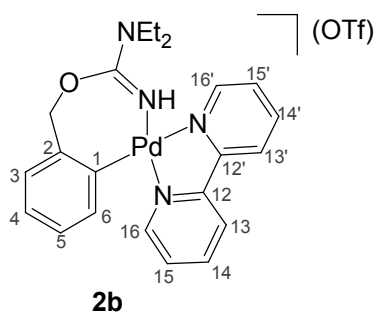


<sup>1</sup>H-RMN spectrum (600 MHz) of **2a**

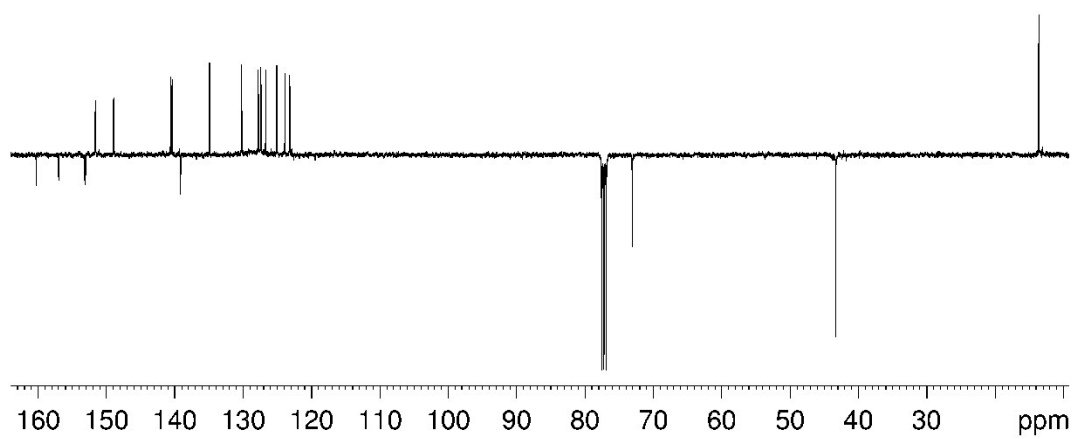


APT spectrum (150.9 MHz) of **2a**

**[Pd{ $\kappa^2$ -C,N-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>OC(=NH)NEt<sub>2</sub>}-2}(bpy)](OTf) (2b)**

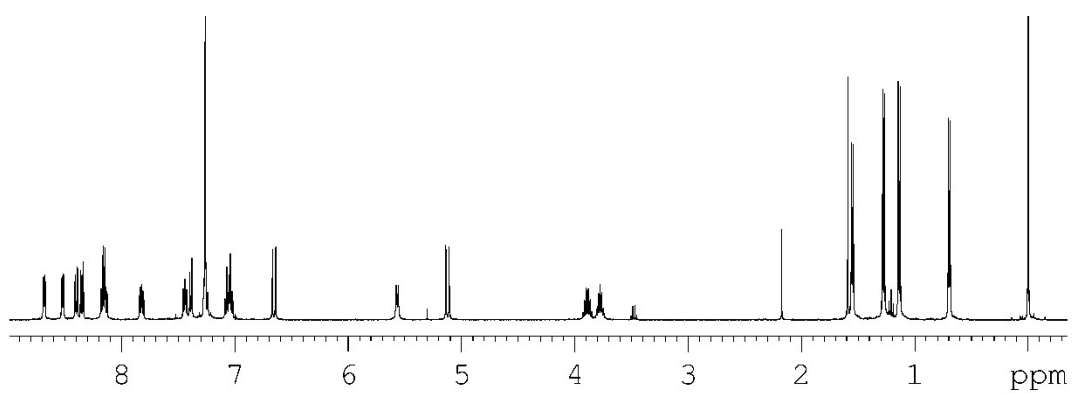
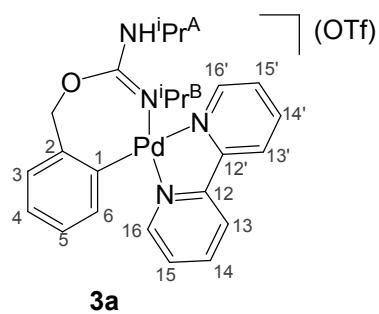


**<sup>1</sup>H-RMN spectrum (400 MHz) of 2b**

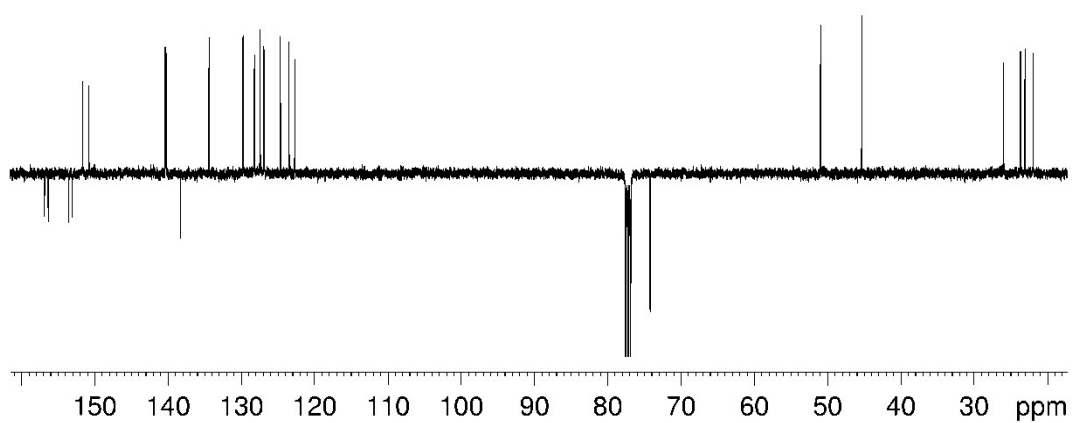


**APT spectrum (100.6 MHz) of 2b**

**[Pd{ $\kappa^2$ -C,N-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>OC(=N<sup>i</sup>Pr)NH<sup>i</sup>Pr}-2}(bpy)](OTf) (3a)**

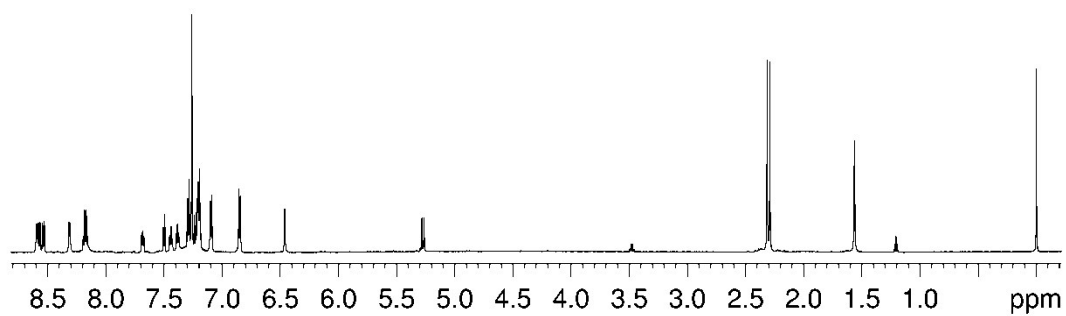
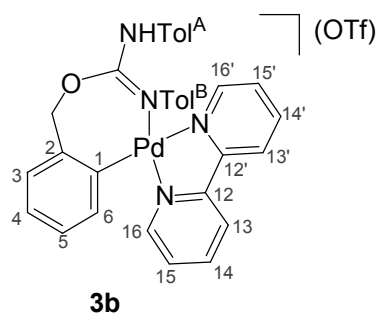


**<sup>1</sup>H-RMN spectrum (400 MHz) of 3a**

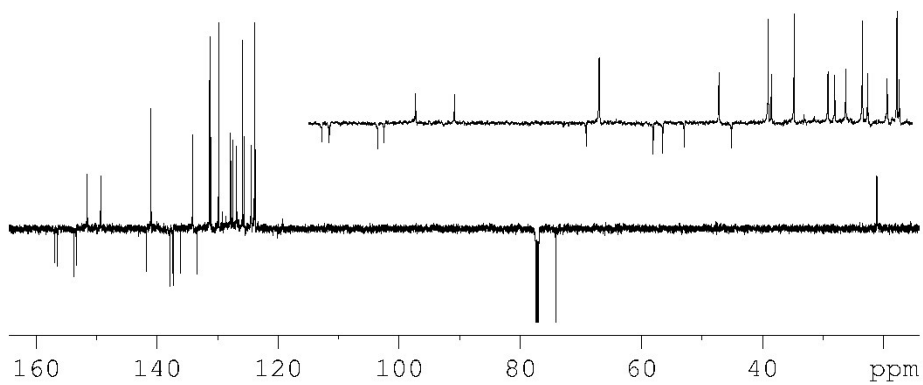


**APT spectrum (100.6 MHz) of 3a**

**[Pd{ $\kappa^2$ -C,N-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>OC(=NTol)NHTol}-2}(bpy)](OTf) (3b)**

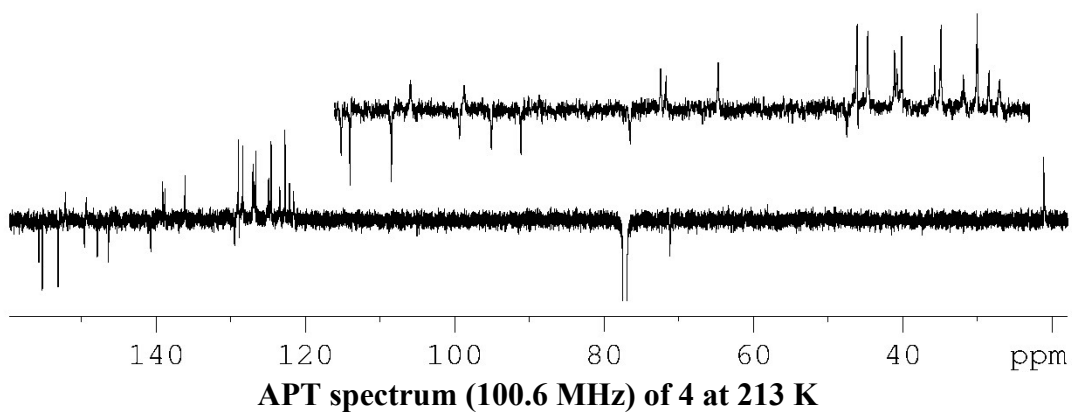
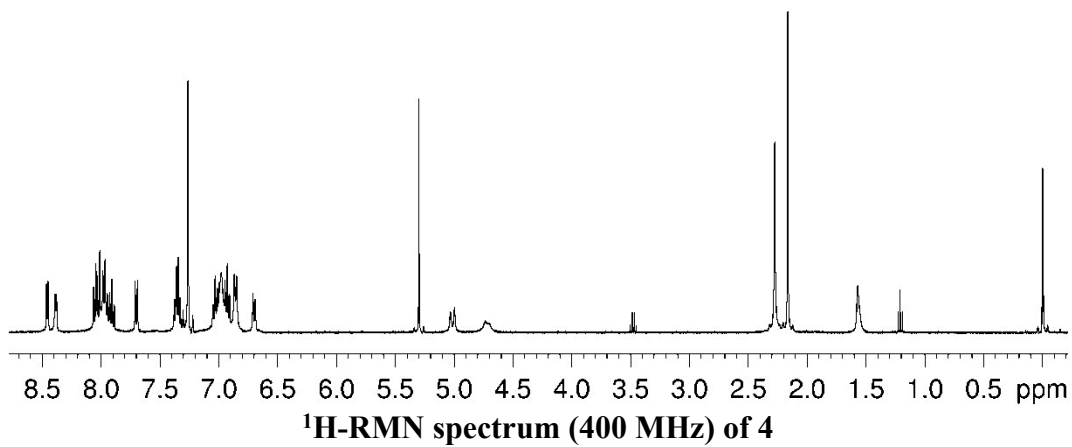
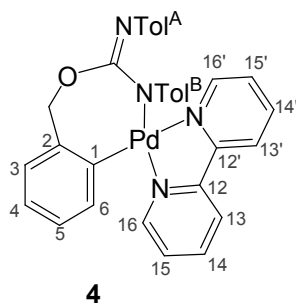


**<sup>1</sup>H-RMN spectrum (600 MHz) of 3b**

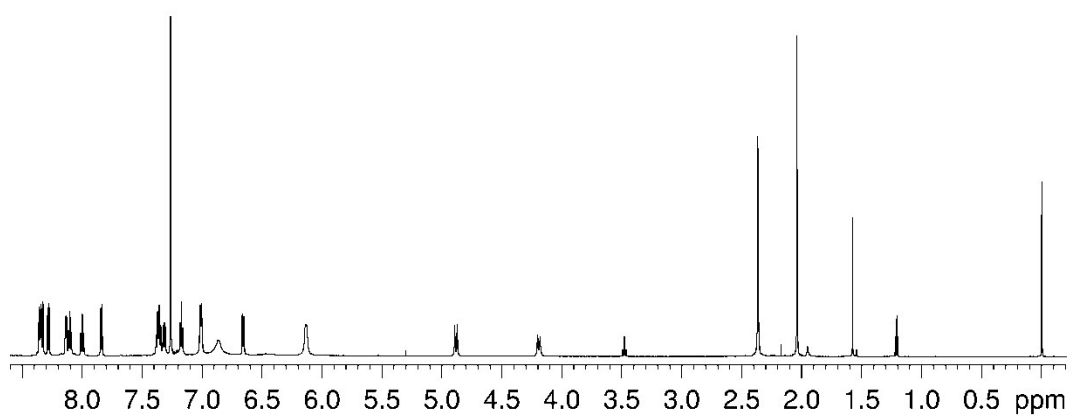
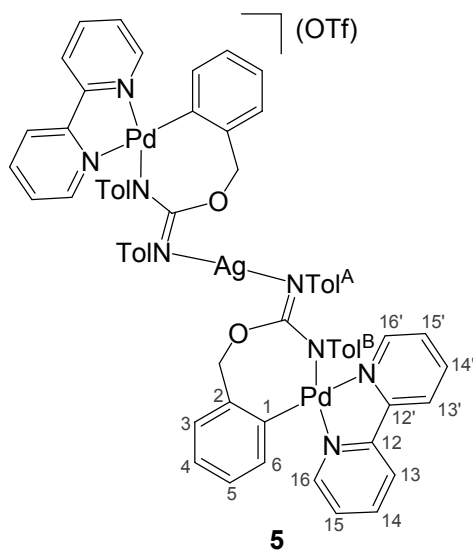


**APT spectrum (150.9 MHz) of 3b**

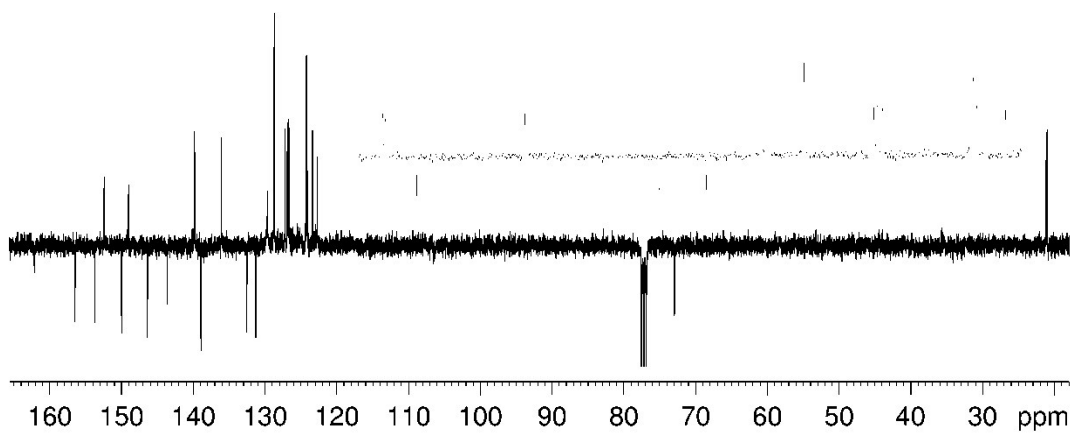
**[Pd{ $\kappa^2$ -C,N-C<sub>6</sub>H<sub>4</sub>{CH<sub>2</sub>OC(=NTol)NTol}-2}(bpy)] (4)**



[Ag(N-4)<sub>2</sub>](OTf) (5)

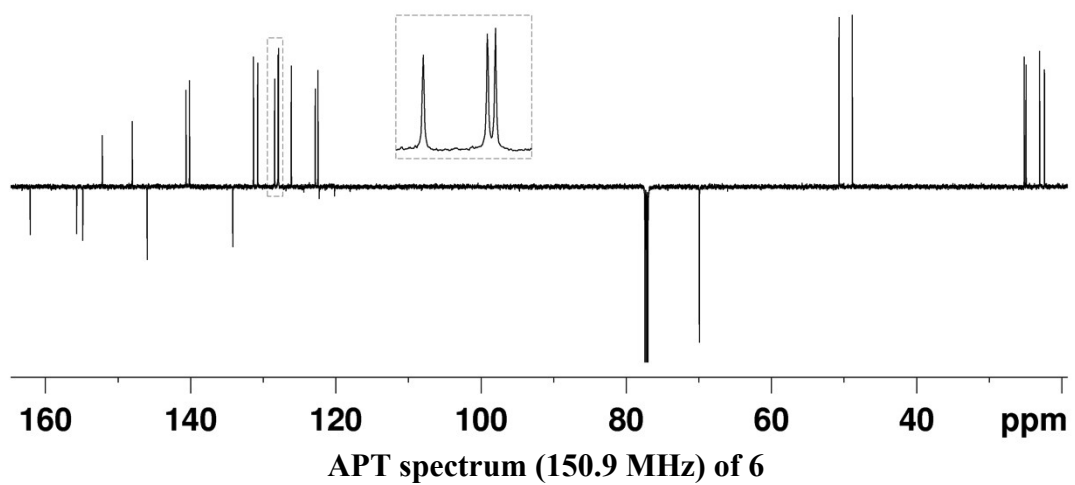
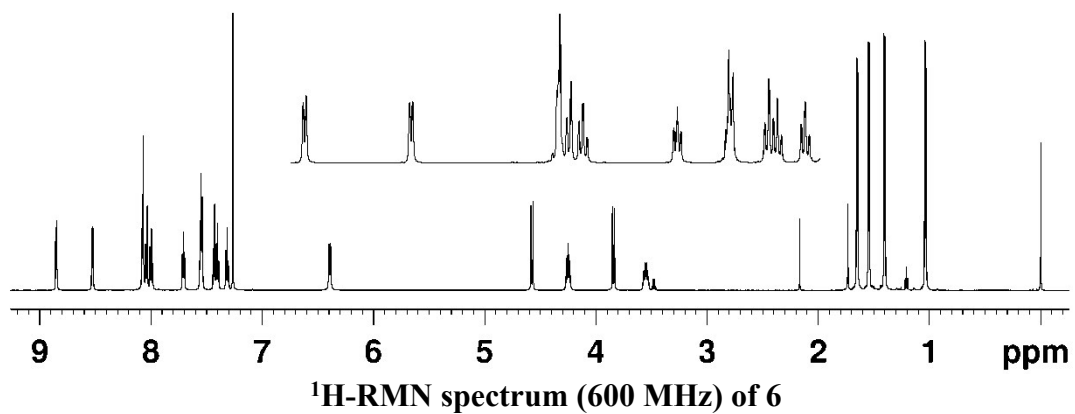
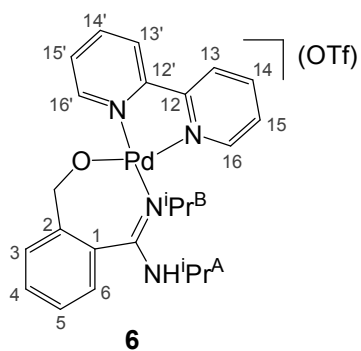


<sup>1</sup>H-RMN spectrum (600 MHz) of 5



APT spectrum (100.6 MHz) of 5

**[Pd{ $\kappa^2$ -O,N-OCH<sub>2</sub>{C<sub>6</sub>H<sub>4</sub>{C(=N<sup>i</sup>Pr)NH<sup>i</sup>Pr}-2}}(bpy)](OTf) (6)**





## X-ray structure determinations.

### Experimental

Crystals were mounted in inert oil on glass fibres. Intensity data were recorded on various Bruker or Oxford Diffraction diffractometers using either monochromated Mo  $K\alpha$  or mirror-focused Cu  $K\alpha$  radiation. Absorption corrections were based on multi-scans. NH hydrogens were refined freely; other hydrogen atoms were included using either rigid methyl groups or a riding model. Structures were refined anisotropically on  $F^2$  using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany).

#### *Exceptions and special features:*

Structure **2a**: The triflate ion is disordered over two positions. A difference peak of ca. 2.3 e  $\text{Å}^{-3}$  was tentatively interpreted as a partially occupied water site. It is impossibly close to O3 and therefore was assigned the same occupation factor as the minor triflate component, with which it does not collide. Water H were not located.

Structure **5**: The asymmetric unit contains two molecules of the Pd/Ag complex, two triflates, five chloroforms and one ether. One of the triflates and two of the chloroforms are disordered. The ether has high  $U$  values.

Structure **III**: The crystal was non-merohedrally twinned by  $180^\circ$  rotation about the  $a$  axis. The structure was refined using the 'HKLF 5' method, which involves different reflection classes for non-overlapped and overlapped reflections. Because of the special handling of twinned crystals (e.g. all equivalents are merged during the untwinning process), the numbers of reflections should be treated with caution. The scale factor refined to 0.495(1).

Structure **IV**: The triflate anion is disordered "head-to-toe".

For all disordered groups, appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be interpreted with caution

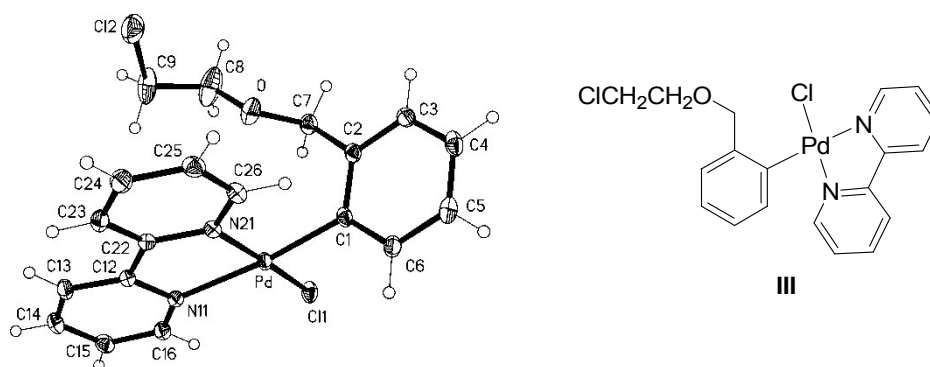
**Table S.2.** X-ray crystallographic data for compounds **2a**, **3a**, **5**, **III**, and **IV**.

	<b>2a</b> 0.19H <sub>2</sub> O	<b>3a</b>	<b>5</b> 2.5CHCl <sub>3</sub> ·0.5Et <sub>2</sub> O	<b>III</b>	<b>IV</b>
Formula	C <sub>21</sub> H <sub>20.38</sub> F <sub>3</sub> N <sub>4</sub> O <sub>4.19</sub> PdS	C <sub>25</sub> H <sub>29</sub> F <sub>3</sub> N <sub>4</sub> O <sub>4</sub> PdS	C <sub>69.5</sub> H <sub>63.5</sub> AgCl <sub>7.5</sub> F <sub>3</sub> N <sub>8</sub> O <sub>5.5</sub> Pd <sub>2</sub> S	C <sub>19</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>2</sub> OPd	C <sub>22</sub> H <sub>21</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>4</sub> PdS
<i>M<sub>r</sub></i>	591.29	644.98	1774.39	467.65	622.33
<i>T</i> (K)	100(2)	103(2)	103(2)	133(2)	100(2)
$\lambda$ (Å)	1.54184	0.71073	1.54184	0.71073	0.71073
cryst syst	Triclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic
space group	<i>P</i> $\bar{1}$	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P2<sub>1</sub>/n</i>	<i>P</i> $\bar{1}$
cell constants					
<i>a</i> (Å)	7.5154(2)	7.9720(2)	12.8921(7) Å	9.132(2) Å	8.0300(4) Å
<i>b</i> (Å)	9.8002(3)	17.9802(5)	17.7080(10) Å	11.578(2) Å	9.1108(4) Å
<i>c</i> (Å)	15.6928(5)	36.9522(10)	33.077(2) Å	17.024(3) Å	16.7796(8) Å
$\alpha$ (deg)	93.082(3)	90	84.739(5)	90	96.350(4)
$\beta$ (deg)	93.631(3)	90	86.381(5)	91.879(8)	98.048(4)
$\gamma$ (deg)	101.326(3)	90	79.154(5)	90	107.239(4)
<i>V</i> (Å <sup>3</sup> ), <i>Z</i>	1128.44(6), 2	5296.7(2), 8	7376.9(7), 4	1798.9(6), 4	1145.78(9), 2
$\rho$ (calcd) (Mg m <sup>-3</sup> )	1.740	1.618	1.598	1.727	1.804
abs. coef. (mm <sup>-1</sup> )	8.070	0.840	9.284	1.338	1.079
<i>F</i> (000)	594	2624	3560	936	624
cryst size (mm)	0.25 x 0.15 x 0.03	0.28 x 0.25 x 0.06	0.10 x 0.08 x 0.05	0.40 x 0.23 x 0.20	0.40 x 0.25 x 0.08
$\theta$ range (deg)	4.61 - 75.70	2.78 - 30.51	3.49 - 76.49	2.13 - 30.54	2.37 - 30.99
	-9 $\leq h \leq$ 9	-11 $\leq h \leq$ 9	-16 $\leq h \leq$ 16	-13 $\leq h \leq$ 12	-11 $\leq h \leq$ 11
index ranges	-12 $\leq k \leq$ 10	-25 $\leq k \leq$ 25	-19 $\leq k \leq$ 22	0 $\leq k \leq$ 16	-13 $\leq k \leq$ 13
	-19 $\leq l \leq$ 19	-52 $\leq l \leq$ 52	-41 $\leq l \leq$ 41	0 $\leq l \leq$ 24	-24 $\leq l \leq$ 24
reflections collected	45759	140731	135416	5343	43722

independent reflections	4664	8074	30575	5452	7294
$R_{\text{int}}$	0.0643	0.0512	0.0837	0.0000	0.0293
abs corr	semi-empirical from equivalents	semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
transmissions	1.00000 - 0.24636	1.00000 - 0.92996	1.00000 - 0.88379	0.8622 - 0.7557	1.00000 - 0.83340
refinement method	full-matrix least squares on $F^2$	full-matrix least squares on $F^2$	locked full-matrix least squares on $F^2$	full-matrix least squares on $F^2$	full-matrix least squares on $F^2$
no. of data/restraints/params	4664 / 79 / 346	8074 / 0 / 351	30575 / 943 / 1836	5452 / 0 / 227	7294 / 116 / 351
goodness-of-fit on $F^2$	1.071	1.019	1.056	1.086	1.050
Final $R$ indices ( $I > 2\sigma(I)$ )					
$R1$	0.0363	0.0254	0.0652	0.0341	0.0209
$wR2$	0.0976	0.0599	0.1679	0.0827	0.0517
R indices (all data)					
$R1$	0.0369	0.0420	0.0965	0.0395	0.0254
$wR2$	0.0981	0.0619	0.1841	0.0851	0.0524
largest diff peak ( $e \text{ \AA}^{-3}$ )	0.776	0.447	2.639	1.270	0.771
largest diff hole ( $e \text{ \AA}^{-3}$ )	1.402	0.701	-1.586	-0.802	-0.838

### Structure of III

The X-ray structure of **III** shows a distorted square planar coordination around the Pd atom, with a mean deviation from the best plane through Pd and the four donor atoms of 0.02 Å. The Pd-C(1) bond distance of 1.981(3) Å is in the range expected for Pd-C bonds *trans* to a N-donor ligand (ca. 1.97-2.00 Å).<sup>1,2,4</sup> The Pd-N(11) (2.121(3) Å) and Pd-N(21) (2.059(3) Å) bond lengths follow the expected order of *trans* influence: Pd-N *trans* to aryl > Pd-N *trans* to Cl. The Pd-Cl(1) bond length of 2.2977(9) Å is in the range found for other aryl palladium complexes with bpy and a chloro ligand (ca. 2.28-2.31 Å).<sup>7</sup> The C(9)-Cl(2) bond distance of 1.795(6) Å is close to the reported value of 1.790 Å for CH<sub>2</sub>-Cl bonds.<sup>8</sup>



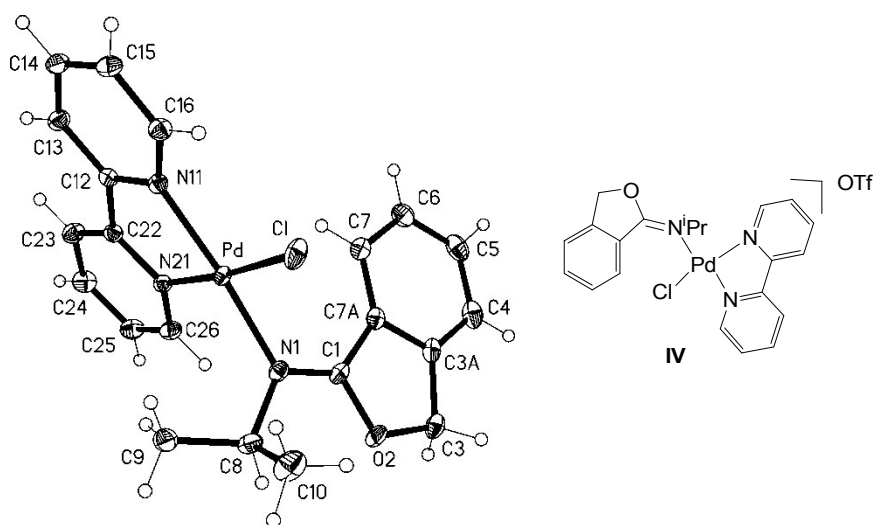
**Figure S.2.** Thermal ellipsoid plot (50% probability level) of **III**.

**Table S.3.** Selected bond lengths (Å) and angles (deg) of **III**.

Pd-C(1)	1.981(3)	C(1)-Pd-N(21)	93.77(12)
Pd-N(11)	2.121(3)	C(1)-Pd-Cl(1)	89.76(10)
Pd-N(21)	2.059(3)	N(11)-Pd-N(21)	78.97(11)
Pd-Cl(1)	2.2977(9)	N(11)-Pd-Cl(1)	97.36(8)
C(1)-C(2)	1.411(5)	N(11)-Pd-C(1)	172.28(12)
C(2)-C(7)	1.497(5)	N(21)-Pd-Cl(1)	175.54(8)
C(7)-O	1.424(4)	C(2)-C(7)-O	108.9(3)
O-C(8)	1.417(6)	C(7)-O-C(8)	110.7(4)
C(8)-C(9)	1.456(7)	O-C(8)-C(9)	111.2(5)
C(9)-Cl(2)	1.795(6)	C(8)-C(9)-Cl(2)	111.4(5)

## Structure of IV

The structure of **IV** shows a distorted square planar coordination around the Pd atom, with a mean deviation from the best plane through Pd and the four donor atoms of 0.04 Å. The three Pd-N bond distances are very similar, Pd-N(1), 2.0373(11) Å; Pd-N(21), 2.0338(11) Å; and Pd-N(11), 2.0210(11) Å, and shorter than the Pd-N bond distances for N-donor ligands *trans* to aryl (between 2.1039(15) and 2.160(4) Å) recently reported by us.<sup>1</sup> The Pd-Cl bond length of 2.2914(4) Å is very similar to that of **III** (2.2977(9) Å) and in the range found for other aryl palladium complexes with bpy and a chloro ligand (ca. 2.28-2.31 Å).<sup>7</sup> The coordination of the iminic nitrogen to Pd leads to a slight lengthening of the C=N bond (1.2890(17) Å) with respect to the mean value in imines (1.279 Å).<sup>8</sup>



**Figure S.3.** Thermal ellipsoid plot (50% probability level) of **IV**.

**Table S.4.** Selected bond lengths (Å) and angles (deg) of **IV**

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Pd-N(1)	2.0373(11)	N(1)-Pd-N(21)	96.50(4)
Pd-N(11)	2.0210(11)	N(1)-Pd-Cl	88.17(3)
Pd-N(21)	2.0338(11)	N(11)-Pd-N(21)	80.66(4)
Pd-Cl	2.2914(4)	N(11)-Pd-Cl	94.78(3)
N(1)-C(1)	1.2890(17)	N(11)-Pd-N(1)	175.39(5)
C(1)-C(7A)	1.4633(19)	N(21)-Pd-Cl	175.05(3)
C(1)-O(2)	1.3517(16)	Pd-N(1)-C(1)	124.05(10)
O(2)-C(3)	1.4571(16)	Pd-N(1)-C(8)	118.57(8)
C(3)-C(3A)	1.496(2)	N(1)-C(1)-O(2)	119.96(12)
		N(1)-C(1)-C(7A)	130.51(12)
		C(1)-O(2)-C(3)	110.44(11)
		O(2)-C(3)-C(3A)	103.91(11)

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