

## Supporting Information

### A Simple Route to the Doubly *ortho*-Palladated Azobenzenes: Building Blocks for Organometallic Polymers and Metallomesogens

*Manda Ćurić, \* Darko Babić, Aleksandar Višnjevac and Krešimir Molčanov*

Institute Ruđer Bošković, Bijenička c. 54, HR-1000 Zagreb, Croatia

#### Table of Contents:

1. Experimental procedures	S1-S2
2. Reaction scheme	S2
3. <sup>1</sup> H and <sup>13</sup> C NMR data (Figure S1, Tables S1 and S2)	S3-S5
4. Crystallographic parameters (Table S3)	S6
5. Ab initio calculations (Tables S4 and S5)	S7
6. References	S8
7. Archived results of <i>ab initio</i> calculations	separate file

## Experimental procedures

All chemicals and solvents used for the syntheses were commercially available. The yields of prepared complexes are based on azobenzenes since Pd is used in excess.

Preparation of  $\{\text{PdCl}(\text{dmf})\}_2(\mu\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)$  (**1**).  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (213 mg, 0.82 mmol) was dissolved in (3 mL) dimethylformamide (dmf) and added to a solution (2 mL) of azobenzene in dmf (50 mg, 0.27 mmol). The mixture was stirred at room temperature for three days and then a new dmf solution (2 mL) of  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (142 mg, 0.55 mmol) was added. The stirring of the resulting mixture continued for three more days. The dark red precipitate was filtered off and dried under vacuum. Yield 70%. Anal. Calcd. (found) for  $\text{C}_{18}\text{H}_{22}\text{N}_4\text{O}_2\text{Pd}_2\text{Cl}_2$ : C, 35.43 (34.90); H, 3.61 (3.50); N, 9.18 (8.98).

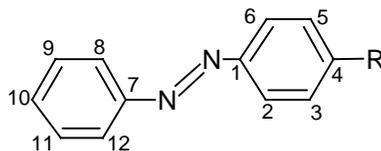
Preparation of  $\{\text{PdCl}(\text{dmf})\}_2(\mu\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_3\text{NH}_2)$  (**2**).  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (197 mg, 0.76 mmol) was dissolved in (3 mL) dmf and added to a solution (2 mL) of azobenzene in dmf (50 mg, 0.25 mmol). The mixture was stirred at room temperature for three days and then a new dmf solution (2 mL) of  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (131 mg, 0.51 mmol) was added. The stirring of the resulting mixture continued for three more days. The brown red precipitate was filtered off and dried under vacuum. Yield 90%. Anal. Calcd. (found) for  $\text{C}_{18}\text{H}_{23}\text{N}_5\text{O}_2\text{Pd}_2\text{Cl}_2$ : C, 34.58 (34.13); H, 3.68 (3.20); N, 11.21 (10.88).

Preparation of  $\{\text{PdCl}(\text{dmsO})\}_2(\mu\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4)$  (**3**). The complex **1** (50 mg, 0.08 mmol) was dissolved in (30 mL) warm dimethyl sulfoxide (dmsO). The solution was filtered off and allowed to stand at room temperature for one week. The red crystals were obtained in a yield 55%. Anal. Calcd. (found) for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_2\text{Pd}_2\text{Cl}_2$ : C, 30.98 (30.82); H, 3.23 (3.50); N, 4.52 (4.26).

Preparation of  $\{\text{PdCl}(\text{dmsO})\}_2(\mu\text{-C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_3\text{NH}_2)$  (**4**). The complex **2** (50 mg, 0.08 mmol) was dissolved in warm dmsO (30 mL). The solution was filtered off and allowed to stand at room temperature for four weeks. The brown red crystals were obtained in a yield 63%. Anal. Calcd. (found) for  $\text{C}_{16}\text{H}_{21}\text{N}_3\text{S}_2\text{O}_2\text{Pd}_2\text{Cl}_2$ : C, 30.24 (29.90); H, 3.31 (3.48); N, 6.62 (6.98).

**NMR spectra.** The one- and two-dimensional  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{dmsO-d}_6$  and/or in  $\text{dmf-d}_7$  with Bruker AV-600 spectrometer, operating at 600.13 for the  $^1\text{H}$  and 150.90 MHz for the  $^{13}\text{C}$  resonances. The  $^1\text{H}$ - $^1\text{H}$  COSY spectra were obtained in the magnitude mode with 2048 points in the *F2* dimension and 512 increments in the *F1* dimension. The  $^1\text{H}$ - $^{13}\text{C}$  HMQC spectra were measured with one-bond C,H coupling value set to 145 Hz, using 2048 points in the *F2* dimension and 256 increments in the *F1* dimension. The  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectra were measured with C,H coupling value set to 145 and 8 Hz using 2048 points in the *F2* dimension and 256 increments in the *F1*





**Figure S1.** The atom numbering of azobenzenes used in the assignment of NMR resonances.

**Table S1.**  $^1\text{H}$  NMR data in DMSO ( $\delta$  ppm,  $J$  Hz)

H	Compound <sup>a</sup>			
	azb <sup>b</sup>	aazb <sup>c</sup>	1 <sup>d</sup> (3) <sup>f</sup>	2 <sup>e</sup> (4) <sup>f</sup>
<b>H-2</b>	7.89 d $J(\text{HH})=6.9$	7.68 d $J(\text{HH})=8.4$		
<b>H-3</b>	7.60 t $J(\text{HH})=7.0$	6.70 d $J(\text{HH})=8.5$	8.74 d $J(\text{HH})=7.2$	7.04 s
<b>H-4</b>	7.58 t $J(\text{HH})=6.6$		7.24 t $J(\text{HH})=7.9$	
<b>H-5</b>	7.60 t $J(\text{HH})=7.0$	6.70 d $J(\text{HH})=8.5$	7.21 t $J(\text{HH})=7.4$	6.35 d $J(\text{HH})=8.9$
<b>H-6</b>	7.89 d $J(\text{HH})=6.9$	7.68 d $J(\text{HH})=8.4$	7.87 d $J(\text{HH})=7.3$	8.41 d $J(\text{HH})=9.1$
<b>H-8</b>	7.89 d $J(\text{HH})=6.9$	7.75 d $J(\text{HH})=7.8$		
<b>H-9</b>	7.60 t $J(\text{HH})=7.0$	7.50 t $J(\text{HH})=7.6$	8.74 d $J(\text{HH})=7.2$	8.22 d $J(\text{HH})=7.9$
<b>H-10</b>	7.58 t $J(\text{HH})=6.6$	7.41 t $J(\text{HH})=7.4$	7.24 t $J(\text{HH})=7.9$	7.03 t $J(\text{HH})=7.7$
<b>H-11</b>	7.60 t $J(\text{HH})=7.0$	7.50 t $J(\text{HH})=7.6$	7.21 t $J(\text{HH})=7.4$	6.84 t $J(\text{HH})=7.6$
<b>H-12</b>	7.89 d $J(\text{HH})=6.9$	7.75 d $J(\text{HH})=7.8$	7.87 d $J(\text{HH})=7.3$	7.65 d $J(\text{HH})=8.0$
<b>NH<sub>2</sub></b>		6.00 s, br		7.51 s, br

<sup>a</sup>Two phenyl rings in azobenzene and its complexes are equivalent.

<sup>b</sup>azb=azobenzene, <sup>c</sup>aazb=4-aminoazobenzene.

<sup>d</sup>(1)={PdCl(dmf)}<sub>2</sub>( $\mu$ -C<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>4</sub>), <sup>e</sup>(2)={PdCl(dmf)}<sub>2</sub>( $\mu$ -C<sub>6</sub>H<sub>4</sub>N=NC<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>).

<sup>f</sup>By dissolving complexes **1** and **2** in dmsO-d<sub>6</sub>, molecules of dmf-h<sub>7</sub> are replaced with dmsO-d<sub>6</sub> forming complexes **3** and **4**, respectively. The signals corresponding to free dmf-h<sub>7</sub> were observed in the spectra of complexes **1** and **2**.

**Table S2.**  $^{13}\text{C}$  NMR data in DMSO ( $\delta$ / ppm)

<b>C</b>	<b>Compound<sup>a</sup></b>			
	<b>azb</b>	<b>aazb</b>	<b>1<sup>b</sup> (3)</b>	<b>2<sup>b</sup> (4)</b>
<b>C-1</b>	152.0	142.8	143.0	149.2
<b>C-2</b>	122.16	125.0	159.0	155.3
<b>C-3</b>	129.5	113.3	128.6	122.0
<b>C-4</b>	131.6	152.4	126.0	153.5
<b>C-5</b>	129.5	113.3	131.6	111.8
<b>C-6</b>	122.2	125.0	136.5	131.2
<b>C-7</b>	152.0	152.7	143.0	142.7
<b>C-8</b>	122.2	121.6	159.0	160.6
<b>C-9</b>	129.5	129.0	128.6	122.0
<b>C-10</b>	131.6	129.2	126.0	124.8
<b>C-11</b>	129.5	129.0	131.6	125.3
<b>C-12</b>	122.2	121.6	136.5	135.4

<sup>a</sup>Two phenyl rings in azobenzene and its complexes are equivalent.

<sup>b</sup>The signals corresponding to free dmf-h<sub>7</sub> or dmsO-h<sub>6</sub> were also observed in the spectra of complexes.

**Table S3.** Crystallographic parameters

<b>Compound</b>	<b>1</b>	<b>4</b>
Molecular formula	C <sub>18</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub> Pd <sub>2</sub>	C <sub>16</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub> Pd <sub>2</sub> S <sub>2</sub>
$M_r$	610.14	636.25
$T(^{\circ}\text{C})$	20	20
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a / \text{\AA}$	12.7700(10)	12.1444(5)
$b / \text{\AA}$	5.2796(6)	6.2403(2)
$c / \text{\AA}$	15.4190(8)	13.8844(7)
$\beta / ^{\circ}$	92.460(10)	95.021(3)
$V / \text{\AA}^3$	1038.60(15) $\text{\AA}^3$	1048.19(8)
$Z$	2	2
$D_x / \text{g cm}^{-3}$	1.951	2.016
Crystal colour and form	red needle	red needle
Crystal dimensions (mm)	0.02 x 0.02 x 0.12	0.02 x 0.05 x 0.12
$\mu$ (Cu- $K_{\alpha}$ ) / $\text{mm}^{-1}$	16.53	18.203
Absorption correction	$\Psi$ -scan	$\Psi$ -scan
Total data	2271	2308
Unique data	2183	2205
Observed data	1721	1691
$R_{\text{int}}$	0.0425	0.0254
$\theta_{\text{max}} / ^{\circ}$	76.44	76.53
$hkl$ limits	-16,16; 0,6; -19,0	-15,0; -7,0; -17,17
$R_1 [F_o > 4\sigma(F_o)]$	0.0480	0.0415
$wR_2 (F^2)$ , all data	0.1409	0.1148
Goodness of fit, $S$	1.061	1.033
Number of variables	133	129

**Table S4.** Comparison of experimental and calculated bond lengths (in Å) around Pd-atom

<b>1</b>					
	X-ray	RHF/B1 <sup>a</sup>	B3LYP/B1 <sup>a</sup>	RHF/B2 <sup>b,c</sup>	B3LYP/B2 <sup>b,c</sup>
Pd-C	1.937	1.994	1.978	1.981	1.968
Pd-N	2.067	2.216	2.102	2.240	2.128
Pd-O	2.192	2.201	2.246	2.254	2.279
Pd-Cl	2.294	2.428	2.402	2.396	2.360
<b>4</b>					
	X-ray <sup>d</sup>	RHF/B1 <sup>a,d</sup>	B3LYP/B1 <sup>a,d</sup>	RHF/B2 <sup>b,d</sup>	B3LYP/B2 <sup>b,d</sup>
Pd-C	1.952	1.998	1.981	1.984	1.967
		1.996	1.983	1.981	1.969
Pd-N	2.055	2.199	2.096	2.224	2.120
		2.211	2.098	2.232	2.123
Pd-O	2.178	2.177	2.194	2.228	2.248
		2.187	2.209	2.240	2.267
Pd-Cl	2.315	2.442	2.423	2.407	2.378
		2.438	2.418	2.405	2.373
S=O	1.524	1.685	1.722	1.521	1.550
		1.686	1.722	1.521	1.550
C-NH <sub>2</sub>	1.250	1.378	1.385	1.375	1.374

<sup>a</sup>B1 denotes smaller basis set with Los Alamos ECP and DZ basis on Pd, S and Cl atoms and D95V basis on all other atoms.

<sup>b</sup>B2 denotes larger basis set with Los Alamos pseudopotential and DZ basis only on Pd atoms and 6-31G(d,p) basis on all other atoms.

<sup>c</sup>Geometry optimization with  $C_i$  symmetry yielded one small negative frequency less than 10 cm<sup>-1</sup>.

<sup>d</sup>Geometry obtained by X-ray diffraction has pseudo  $C_i$  symmetry (not really present in the molecule). Calculated distances are shown for both pseudosymmetrical bonds, first for those around Pd-atom linked to aromatic ring with NH<sub>2</sub> bond.

**Table S5.** Calculated energies of all configurational isomers of **3**<sup>a,b</sup> in Hartrees.

	O-Pd/O-Pd	O-Pd/S-Pd	S-Pd/O-Pd	S-Pd/S-Pd
<i>cis/cis</i>	-2851.6438	-2851.6386	-	-2851.6336
<i>cis/trans</i>	-2851.6503	-2851.6368	-2851.6455	-2851.6314
<i>trans/trans</i>	-2851.6583	-2851.6441	-	-2851.6296

<sup>a</sup>Rows indicate positions of dmsO in respect to Pd-C bonds on two sides of the complex, and columns indicate the heteroatom by which dmsO was bound to Pd atom.

<sup>b</sup>Energies are corrected for zero point of energy (ZPE).

## References:

- (1) Farrugia, L. J. *J. Appl. Cryst.*, **1999**, 32, 837.
- (2) Sheldrick, G. M. SHELX97, **1997**. Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany.
- (3) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
- (4) Dunning Jr, T. H.; Hay, P. J., In *Modern Theoretical Chemistry*, Schaefer III, H. F., Ed.; Plenum: New York, 1976, 3, 1.
- (5) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, 82, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, 82, 299.