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Electronic Supporting Information

for the manuscript entitled

Pd(II) complexes with amide-based macrocycles: Syntheses, properties, and application in cross-coupling reactions

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Weak interactions in the crystal structures of 1 - 4. The solid state packing of complex 1 is comprised of several weak CH...O and CH...C interactions (Figure 2a). This complex is engaged in self-complimentary C–H...O interactions involving O_{amide} atom of one molecule and hydrogen atoms of the –CH₂– fragments from the adjacent molecule (C–H14A...O2 and C–H12B...O2) that results in the generation of a dimer. Such dimers are further engaged in intermolecular C–H...O interactions between O_{amide} atom and the methylene proton (C–H11A...O2); and O_{amide} (O1) with methyl proton (C–H13B...O1) as well as with methylene proton (C–H12A...O1). Such interactions result in the formation of a one–dimensional zig – zag chain. Two such chains are further connected to each other via C–H...O bonds involving O_{amide} and hydrogen atom from the phenylene ring (C–H3...O1) (Figure S3). There also exist several CH...C interactions within the dimer as well as between the dimers. The table S1 lists several such intra– and inter–molecular hydrogen bonding interactions that are present in complex 1.

The packing of complex **2** is similar to that of complex **1** with additional weak interactions involving the –Cl atoms (Figures 2b and S4). As noted for complex **1**, complex **2** also forms a dimer via self-complimentary C–H...O interactions between O_{amide} and the methylene group from the adjacent molecule (C–H8B...O1). Such dimers are further engaged in intermolecular C–H...O interactions involving O_{amide} with methyl (C–H9C...O1); and methylene (C–H10B...O1) protons. The second O_{amide} atom forms an inter–molecular H–bond with the methyl proton (C–H13B...O2) and thus generates a 2D layer. Within a 2D layer, one of the chloride atoms interacts with the methyl proton (C–H13A...Cl2). Furthermore, both intra– and inter–molecular C–H...C interactions exist within and between the dimers (Table S1).

The complex **3** again shows the creation of a dimer as noted earlier. Figure 2c shows such a dimer formation through self-complementary C–H...O interaction between O_{amide} and methylene proton from the adjacent molecule (C–H8B...O1). These dimers are further engaged in several intra– and inter–molecular C–H...C interactions (Figure S5). In addition, another C–H...O hydrogen bonding interaction exists between O_{amide} and hydrogen atoms of the methyl group present on the arene ring (C–H17A...O1). Further, O_{amide} atom forms H–bond with the

methylene (C-H12A...O2) and methyl proton (C-H13B...O2), respectively.

Complex 4 forms a dimer via self-complimentary C–H...O interaction between O_{amide} and hydrogen atoms from the methylene groups (C–H12B...O2 and C–H14A...O2) in addition to several weak C–H...C interactions (Figures 2d and S6). Complex 4 also shows C–H...O interaction involving $O_{methoxy}$ atom and hydrogen atom of the methyl group from the adjacent molecule (C–H9B...O3). Finally, the O_{amide} atom from one of the parallel running chains makes H–bond with the methoxy group proton (C–H16A...O2) thus connecting two such chains (Figure S6).



Figure S1. Absorption spectra of complexes 1 - 4 in DMF. Inset shows the expanded portion of the spectra between 270 - 500 nm.



Figure S2. Combined ¹H NMR spectra of palladium complexes 1 - 4 in [D₆]-DMSO at 25°C.



Figure S3. 3D linear chain formation view through C–H...C and C–H...O hydrogen bonding interactions in complex **1**. All hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.



Figure S4. View of 3D chain arrangement via C–H...O and C–H...C weak interactions for complex **2**. All hydrogen atoms except those involved in hydrogen bonding are omitted for clarity.



Figure S5. View of 2D chain formation via C–H...C, C–H...N and C–H...O hydrogen bonding interaction for complex **3**. All hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.



Figure S6. View of formation of 2D bimolecular chain through C–H...C and C–H...O hydrogen bonding interaction for complex **4**. All hydrogen atoms except those involved in hydrogen bonding are omitted for clarity.



Figure S7. Time-dependent absorption spectra of species $[4^{O_X}]^+$ after chemical oxidation using $(NH_4)_2[Ce(NO_3)_6]$ in DMF.



Figure S8. EPR spectrum of species $[4^{Ox}]^+$ after chemical oxidation using $(NH_4)_2[Ce(NO_3)_6]$ in DMF.



Figure S9. The Heck coupling reaction between iodobenzene and styrene in DMF using complex **2** as the catalyst. In this reaction, "<u>four</u>" consecutive batches of iodobenzene and styrene were added within the same reaction vessel containing complex **2**. In all four cases; the overall conversion (*cis* + *trans* products) remained unchanged which is evident from a = b = c = d. Reactions conditions were identical as mentioned in Table 5.



Figure S10. ¹H NMR spectrum of Butyl-3-*p*-tolylacrylate recorded in CDCl₃.



Figure S11. ¹³C NMR spectrum of Butyl-3-*p*-tolylacrylate recorded in CDCl₃.



Figure S12. ¹H NMR spectrum of Butyl-3-(4-methoxyphenyl)acrylate recorded in CDCl₃.



Figure S13. ¹³C NMR spectrum of Butyl-3-(4-methoxyphenyl)acrylate recorded in CDCl₃.



Figure S14. ¹H NMR spectrum of 1-methyl-4-styrylbenzene recorded in CDCl₃.



Figure S15. ¹H NMR spectrum of 1-methoxy-4-styrylbenzene recorded in CDCl₃.



Figure S16. ¹³C NMR spectrum of 1-methoxy-4-styrylbenzene recorded in CDCl₃.



Figure S17. ¹H NMR spectrum of 4'-(4-Fluorobenzyloxy)-4-methylbiphenyl recorded in CDCl₃.



Figure S18. ¹³C NMR spectrum of 4'-(4-Fluorobenzyloxy)-4-methylbiphenyl recorded in CDCl₃.



Figure S19. ¹H NMR spectrum of 1-nitro-4-styrylbenzene recorded in CDCl₃.



Figure S20. ¹H NMR spectrum of 4-methyl-4'-methoxy-1-styrylbenzene recorded in CDCl₃.



Figure S21. ¹H NMR spectrum of 4-chloro-4'-methoxy-1-styrylbenzene recorded in CDCl₃.



Figure S22. ¹H NMR spectrum of 1-chloro-4-styrylbenzene recorded in CDCl₃.



Figure S23. ¹H NMR spectrum of 4-*tert*-butyl-4'-chloro-1-styrylbenzene recorded in CDCl₃.

Proton	$[Pd(L^{H})](1)$	$[Pd(L^{Cl})](2)$	$[Pd(L^{Me})](3)$	$\left[\mathrm{Pd}(\mathrm{L}^{\mathrm{OMe}})\right](4)$
a/a'	1.23, s	1.27, s	1.22, s	1.23, s
b	2.56, d, <i>J</i> = 13.2	2.78, d, <i>J</i> = 9.5	2.57, d, <i>J</i> = 12.5	2.56, d, <i>J</i> =13.2
b'	2.93, t, J = 11.7	3.09, t, J = 12.4	2.98, t, J = 13.2	2.98, t, J = 12.5
С	3.56, d, <i>J</i> = 15.4	3.60, d, <i>J</i> = 16.1	3.54, d, <i>J</i> = 15.4	3.55, d, <i>J</i> = 16.1
c'	4.09, d, J = 16.1	4.00, d, <i>J</i> = 15.4	4.07, d, <i>J</i> = 15.4	4.11, d, J = 15.4
d	8.10, dd, J = 5.9	8.16, s	7.88, s	7.81, s
е	6.83, dd, $J = 5.9$	-	-	-
Ar-CH ₃	-	-	2.13, s	-
Ar-OCH ₃	-	-	-	3.81, s
$-CH_3$	2.75,s	2.80, s	2.75, s	2.75, s

Table S1.^[a] Proton NMR spectral data for complexes 1, 2, 3 and 4.

[a] Spectra were recorded in CDCl₃. Abbreviations: s = singlet, d= doublet; t = triplet; m = multiplet. [b] Geminal coupling constant

Table S2. Hydrogen	bonding parameters t	for compl	exes $1-4$.
200			

	D····A/Å	H···A/Å	D-H···A /°	
[PdL ^H] (1)				
C3–H3…O1 [-x+1,-y,-z-1]	3.501(6)	2.606(4)	162.20(3)	
C11–H11A····O2 [-x+2,+y+1/2,-z+1/2]	3.220(6)	2.328(3)	152.50(3)	
C12–H12A···O1 [x,-y+1/2,+z+1/2]	3.560(7)	2.656(4)	155.08(3)	
C12–H12B···O2 [-x+2,-y,-z]	3.577(7)	2.693(4)	151.70(3)	
C13–H13B···O1 [x,-y+1/2,+z+1/2]	3.515(6)	2.650(4)	150.43(3)	
C14–H14A…O2 [-x+2,-y,-z]	3.310(7)	2.409(4)	153.21(4)	
C8–H8B···C1 [-x+2,-y,-z]	3.839(7)	2.877(4)	171.76	
C10–H10A···C5 [-x+2,-y,-z]	3.778(8)	2.889(5)	152.92	
C10–H10A···C6 [-x+2,-y,-z]	3.763(8)	2.795(5)	175.57	
C13–H13C···C1 [-x+1,-y,-z]	3.333(8)	2.811(5)	115.13	
C13–H13A···C6 [-x+1,-y,-z]	3.235(7)	2.876(5)	103.22	

$[PdL^{Cl}]$ (2) C8-H8B…O1 3.384(5)154.61(3) 2.485(3)[-x, -y, -z]С9-Н9С…О1 3.592(7) 153.52(3) 2.705(4)[x,+y+1,+z]C10-H10B…O1 3.606(6) 2.685(3)157.48(3) [x,+y+1,+z]C13-H13B····O2 3.339(6) 2.415(4) 163.03(3)[x,+y,+z+1]C10-H10A····C2 164.56 3.741(4) 2.842(3)[-x, -y, -z]C12-H12B····C4 2.854(4)133.35 3.592(6) [-x, -y, -z]C12-H12B····C5 3.701(5) 2.864(3)144.85 [-x, -y, -z] C3–Cl1…O2 3.201(4) (4.70)142.47 [x, +y-1, +z] $[PdL^{Me}]$ (3) C8–H8B…O1 3.292(1)2.417(1)149.72(2)[-x+1,-y,-z+1]C10-H10B…N2 3.566(1)2.588(1)173.26(2) [-x+1,+y-1/2,-z+1/2]C12-H12A…O2 3.569(2)2.672(1)154.06(4) [x-1,+y,+z]C13-H13B····O2 3.564(1)2.687(1)151.53(4) [x-1,+y,+z]C17-H17A…O1 132.89(3) 3.334(2)2.606(1)[x+1,+y,+z]C12-H12B…C1 3.815(9) 2.853(7)171.64 [-x+1, -y, -z+1]C12-H12B····C2 3.777(12) 2.883(10)153.69 [-x+1, -y, -z+1]C14-H14A…C6 3.749(13) 2.795(10)168.06 [-x+1, -y, -z+1]С9-Н9С…С1 3.789(11) 2.841(8) 169.33 [-x+1, +y+1/2, -z+1/2] C10-H10B····C6 3.771(10) 2.864(8) 156.16 [-x+1, +y+1/2, -z+1/2] $[PdL^{OMe}]$ (4) C9-H9B---O3 3.551(5) 149.46(3) 2.691(3) [x+1/2,-y+1/2,+z-1/2]

C12–H12B···O2 [-x+2vz+1]	3.544(5)	2.660(3)	151.26(2)
C14–H14A···O2 [-x+2,-y,-z+1]	3.322(5)	2.470(2)	146.94(2)
C16–H16A···O2 [x-1.+y.+z]	2.980(5)	2.512(2)	110.21(3)
C8–H8B···C1 [-x+2vz+1]	3.742(5)	2.773(3)	176.74
C10–H10A···C5 [-x+2,-y,-z+1]	3.648(5)	2.737(3)	156.66
C10–H10A···C6 [-x+2vz+1]	3.735(5)	2.769(3)	174.00
C12-H12A···C1 [-x+1/2+1, +y+1/2, -z+1/2]	3.780(5)	2.863(3)	157.54
$C12-H12A\cdots N1$ [-x+1/2+1 +y-1/2 -z+1/2]	3.704(5)	2.743(3)	171.16
C13–H13B···C1 [-x+1/2+1, +y+1/2, -z+1/2]	3.758(5)	2.893(3)	150.59

Table S3. Cyclic voltammetric data for complexes 1, 2, 3 and 4 and their comparison with analogous Ni(II) and Cu(II) complexes as displayed in Chart 1.

Complex	E_1 (V) in DMF (ΔE_n	E_1 (V) in DMSO	E_1 (V) in MeOH
1	$(\dot{m}\dot{V})\dot{)}$	$(\Delta E_n (mV))$	$(\Delta E_n (mV))$
ED IT UL (4)	0.02 (120)		
$[PdL^{n}](\mathbf{I})$	0.93 (130)	1.02[6]	1.13[0]
$[PdL^{Cl}](2)$	1.20 (120)	1.04 ^[b]	1.06 (120)
$[PdL^{Me}]$ (3)	0.80 (70)	0.84 (100)	0.91 ^[b]
[PdL ^{OMe}] (4	l) 0.58 (60)	0.59 (70)	0.60 (70)
Ī	0.77 (90)		
J	0.84 (70)		
К	0.70 (70)		
\mathbf{L}	0.73 ^[b]		
Μ	0.63 (70)		
Ν	0.75 (74)		
0	0.60 (80)		
Р	0.81 ^[b]		

[a] Conditions: Complex, *ca.* 1mM solution; TBAP as supporting electrolyte, *ca.* 100 mM solution; potential (V) vs SCE; platinum as the working electrode; Pt wire as the auxiliary electrode; scan rate – 100 mV/s. [b] E_{pa} .

	[PdL ^H] (1)	[PdL ^{Cl}] (2)	[PdL ^{Me}] (3)	$[PdL^{OMe}]$ (4)
Empirical formula	$C_{15}H_{20}N_4O_2Pd$	$C_{15}H_{18}Cl_2N_4O_2Pd$	$C_{17}H_{24}N_4O_2Pd$	$C_{17}H_{24}N_4O_4Pd$
Formula weight	394.75	463.63	422.80	454.80
Temperature	293(2)K	293(2)K	293(2)K	293(2)K
Wavelength	0.71073 Å	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P 2_1/c$	P -1	$P 2_1/c$	$P 2_1/n$
а	9.606(2) Å	9.8262(3) Å	9.864(5) Å	10.4774(4) Å
b	15.616(4) Å	9.8965(3) Å	10.537(5) Å	10.9664(3) Å
С	10.6058(11) Å	9.9887(3) Å	17.033(5) Å	16.1533(6) Å
α	90°	104.009(3)°	90°	90°
β	104.624(16)°	99.865(2)°	106.046(5)°	99.730(3)°
γ	90°	110.867(3)°	90°	90°
Volume	1539.3(5) Å ³	845.08(4) Å ³	1701.4(13) Å ³	1829.30(11) Å ³
Ζ	4	2	4	4
Density (calculated)	1.703Mg/m ³	1.822Mg/m ³	1.651Mg/m ³	1.651Mg/m ³
Absorption coefficient	1.218 mm ⁻¹	11.914 mm ⁻¹	8.944 mm ⁻¹	8.452 mm ⁻¹
F (000)	800	464	864	928
Crystal size	0.25 x 0.21 x 0.19 mm ³	0.35 x 0.30 x 0.03 mm ³	0.31 x 0.20 x 0.08 mm ³	0.23 x 0.21 x 0.20 mm ³
Theta range	2.87 to 25.00°	5.02 to 67.50°	4.99 to 67.46°	4.90 to 73.39°
Index ranges	$-11 \le h \le 11, -17 \le k \le 18,$	$-11 \le h \le 11, -11 \le k \le 11,$	$-11 \le h \le 10, -9 \le k \le 12,$	$-11 \le h \le 12, -13 \le k \le 13,$
	$12 \le l \le 9$	$11 \le 1 \le 11$	$20 \le l \le 20$	$19 \le l \le 18$
Reflections collected	5960	12741	4748	8698
Independent collections	2714 [<i>R</i> (int) = 0.0387]	3044 [<i>R</i> (int) = 0.0619]	2680 [R(int) = 0.0314]	3611 [<i>R</i> (int) = 0.0282]
Data completness	99.9%	99.9%	87.2%	98.5%
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
	on F^2	on F^2	on F^2	on F^2
Data / restraints /	2714 / 0 / 199	3044 / 0 / 217	2680 / 0 / 218	3611 / 0 / 235
parameters				
Goodness-of-fit on F ²	1.018	1.056	1.053	1.063
Final R indices	$R_1 = 0.0392, wR_2 =$	$R_1 = 0.0366, wR_2 =$	$R_1 = 0.0589, wR_2 =$	$R_1 = 0.0305, wR_2 =$
[I>2sigma(I)] ^{a,b}	0.0917	0.0923	0.1846	0.0816
R indices (all data)	$R_1 = 0.0540, wR_2 =$	$R_1 = 0.0372, wR_2 =$	$R_1 = 0.0670, wR_2 =$	$R_1 = 0.0349, wR_2 =$
	0.0956	0.0930	0.2052	0.0860
Largest diff. Peak and hole	0.655 and -0.969 e.Å ⁻³	2.029 and -0.599 e.Å ⁻³	1.183 and -1.671 e.Å ⁻³	0.447 and -0.952 e.Å ⁻³

Table S4. X-ray crystallographic data collection and structural refinement parameters for palladium complexes 1 - 4.

[a] $R = \Sigma ||Fo| - |Fc||/\Sigma |Fo|$; [b] $R_w = \{ [\Sigma (|Fo|^2 |Fc|^2)^2] \}^{1/2}$.



Chart 1. Complexes **1**, **2**, **3** and **4** and analogous Ni(II) and Cu(II) complexes with 12-membered macrocyclic ligands¹ and 13-membered macrocyclic ligands.²

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