Table 1S. ^{15}N NMR chemical shifts (δ, ppm) in LL·2HCl and [Pd(LL)Cl$_2$], **1, 2a, 2b** [a)]

Atom	**LL·2HCl**	**[Pd(LL)Cl$_2$]**	**1**	**2a**	**2b**
	δ	**δ (Δδ)**	**δ (Δδ)**	**δ (Δδ)**	**δ (Δδ)**
N^3	-331.5	-367.2 (-35.7)	-379.3 (-47.8)	-360.8 (- 29.3)	-357.5 (-26.0)
N^4	-348.7	-382.0 (-33.3)	-394.9 (-46.2)	-372.4 (-23.7)	-375.9 (-27.2)

a) 10 mM in DMSO-d_6/CD$_3$CN, 1:2 v/v solution. ^{15}N chemical shifts are referenced to external CD$_3$NO$_2$. Parameter Δδ denotes the difference of ^{15}N chemical shifts between the complex and the dihydrochloride of LL

Table 2S. ^{1}H NMR chemical shifts (δ, ppm) and coupling constants (J, Hz) in LL·2HCl and [Pd(LL)Cl$_2$], **1, 2a, 2b** [a)]

δ [ppm]	**LL·2HCl**	**[Pd(LL)Cl$_2$]**	**1**	**2a**	**2b**
H^1	4.81 (bt, ^3J = 3.5)	4.74 (d, ^3J = 3.9)	4.71 (bd, ^3J = 3.5)	4.72	4.75
H^2	2.08$^{b)}$	2.24 (m, ^3J = 3.9, ^2J = 14.0, ^3J = 13.0)	2.15 (ddd, ^2J = 13.5, ^3J = 13.5, ^3J = 3.8)	2.02	2.08
H$^{2'}$	2.08$^{b)}$	1.89 (m, ^2J = 14.0, ^3J = 6.0)	1.86 (dd, ^2J = 13.5,^3J = 5.3)	1.94	1.94
H^3	3.80 (m)	2.97 (m)$^{b)}$	2.87 (m)	3.22	3.23
H^4	3.77 (bd)	3.01 (m)$^{b)}$	2.82 (m)	3.05	3.02
H^5	4.10 (q, ^3J = 6.8)	3.87 (q, ^3J = 6.9)	3.96 (q, ^3J = 6.5)	4.01	4.01
CH$_3$	1.22 (d, ^3J = 6.8)	1.03 (d, ^3J = 6.9)	1.05 (d, ^3J = 6.5)	1.08	1.10
OCH$_3$	3.30 (s)	3.23 (s)	3.21 (s)	3.23	3.24
N^{3}H^c	$^{c)}$	4.94 (bm)	5.47$^{e)}$ (bd)	7.22	6.48
N^{3}H^t	$^{c)}$	4.05 (bd, ^2J = 10.5)	4.87$^{e)}$(bd, ^2J = 10.5)	5.39	5.56
N^{4}H^c	$^{c)}$	4.51 (bm)	5.29$^{f)}$ (bs)	5.96	6.20
N^{4}H^t	$^{c)}$	3.90$^{d)}$	4.31$^{f)}$ (bt, ^2J = 10.5)	5.26	5.66

a) 10 mM in DMSO-d_6/CD$_3$CN, 1:2 v/v solution. ^{1}H chemical shifts are referenced to internal CD$_3$CN, δ = 1.93 ppm
b) Two overlapping multiplets
c) Not resolved due to exchange
d) Broad, hidden under H^5
e) Assignments are based on analogy with **2a** and **2b**, can be interchanged
f) Assignments are based on analogy with **2a** and **2b**, can be interchanged

Table 3S ^{13}C NMR chemical shifts (δ, ppm) in LL·2HCl and [Pd(LL)Cl$_2$], **1, 2a, 2b** $^{a)}$

	LL·2HCl	**[Pd(LL)Cl$_2$]**		**1**		**2a**		**2b**	
	δ	δ	Δδ	δ	Δδ	δ	Δδ	δ	Δδ
C^1	98.0 (171.2)	98.3 (169.3)	0.3	98.01	0.01	98.00	0.00	98.22	0.22
C^2	29.3 (131.3)	30.6 (126.4, 132.8)	1.3	29.88	0.58	29.96	0.66	30.21	0.91
C^3	47.6 (145.1)	54.2 (144.0)	6.6	53.97	6.37	54.00	6.40	54.30	6.70
C^4	52.2 (148.1)	60.3 (143.8)	8.1	61.58	9.38	61.05	8.85	60.85	8.65
C^5	65.1 (147.0)	61.9 (144.4)	-3.2	62.31	-2.79	61.87	-3.23	61.80	-3.30
CH_3	17.7 (127.7)	17.2 (127.2)	-0.5	17.56	-0.14	17.43	-0.27	17.70	0.00
OCH_3	55.3 (142.7)	55.1 (142.3)	-0.2	55.03	-0.27	55.07	-0.23	55.77	0.47

a) 10 mM in DMSO-d_6/CD$_3$CN, 1:2 v/v solution. ^{13}C chemical shifts are referenced to internal CD$_3$CN, δ = 1.28 ppm
Parameter Δδ denotes the difference of ^{13}C chemical shifts between the complex and the dihydrochloride of LL
Coupling constants (^1J(C,H), Hz) are in parentheses.

Table 4S Calculated NMR shieldings [ppm] of **1**-**3** complexes at GIAO DFT level a)

Atom	**1**	**2a’**	**2b’**	**3a**	**3b**
N^3	207.6	198.2	205.7	208.6	217.0
N^4	225.5	222.9	214.9	233.4	226.1
C^1	79.9	80.7	81.2	80.9	80.7
C^2	148.4	148.2	147.9	148.5	148.5
C^3	126.2	125.7	123.1	125.8	123.3
C^4	120.2	118.4	120.7	118.3	120.9
C^5	116.7	116.9	117.1	117.5	117.6
C^{CH3}	165.7	165.8	165.8	166.5	165.8
C^{OCH3}	126.2	124.7	124.7	124.6	124.5
O	241.4	240.2	241.7	240.9	240.2
O^{OCH3}	257.7	257.1	257.8	257.4	257.1
H^1	27.24	26.98	27.00	27.01	27.01
H^2	30.34	29.97	30.09	29.97	29.99
$H^{2'}$	29.58	29.88	29.94	29.92	29.95
H^3	28.66	28.32	28.15	28.27	28.22
H^4	29.45	29.11	29.24	29.25	29.26
H^5	28.00	27.75	27.75	27.69	27.68
H^{CH3}	30.83	30.65	30.63	30.63	30.64
H^{OCH3}	28.53	28.38	28.39	28.34	28.34
H^t at N^3	29.35	28.80	28.95	28.79	28.96
H^c at N^3	30.11	29.40	29.51	29.42	29.55
H^t at N^4	29.31	28.51	28.42	28.64	28.39
H^c at N^4	29.82	29.28	29.21	29.24	29.10
$C^{(DMSO)-Pt}$	-	132.1	131.9	-	-
$H^{(DMSO)-Pt}$	-	28.72	28.74	-	-
O^{H2O-Pt}	-	-	-	362.3	363.5
H^{H2O-Pt}	-	-	-	30.16; 29.63	30.23; 29.60

a) **2a’** and **2b’** denotes position of DMSO-h_6 *trans* to N^4 and *trans* to N^3, respectively; **3a** and **3b** denotes position of H_2O *trans* to N^4 and *trans* to N^3, respectively

Table 5S Calculated NMR chemical shifts [ppm] of **1-3** complexes at GIAO DFT level[a)], in respect to nitromethane (^{15}N) or TMS (^{1}H, ^{13}C).

Atom	**1**	**2a’**	**2b’**	**3a**	**3b**
N^3	-365.0	-355.6	-363.1	-366.0	-374.4
N^4	-382.9	-380.3	-372.3	-390.8	-383.5
C^1	103.6	102.8	102.3	102.6	102.8
C^2	35.1	35.3	35.6	35.0	35.0
C^3	57.3	57.8	60.4	57.7	60.2
C^4	63.3	65.1	62.8	65.2	62.6
C^5	66.8	66.6	66.4	66.0	65.9
C^{CH3}	17.8	17.7	17.7	17.0	17.7
C^{OCH3}	57.3	58.8	58.8	58.9	59.0
H^1	4.66	4.92	4.90	4.89	4.89
H^2	1.56	1.93	1.81	1.93	1.91
$H^{2'}$	2.32	2.02	1.96	1.98	1.95
H^3	3.24	3.58	3.75	3.63	3.68
H^4	2.45	2.79	2.66	2.65	2.64
H^5	3.90	4.15	4.15	4.21	4.22
H^{CH3}	1.07	1.25	1.27	1.27	1.26
H^{OCH3}	3.37	3.52	3.51	3.56	3.56
$C^{(DMSO)\text{-}Pt}$	-	51.4	51.6	-	-
$H^{(DMSO)\text{-}Pt}$	-	3.18	3.16	-	-

[a)] **2a’** and **2b’** denotes position of DMSO-h_6 *trans* to N^4 and *trans* to N^3, respectively; **3a** and **3b** denotes position of H_2O *trans* to N^4 and *trans* to N^3, respectively

Table 6S Selected calculated geometrical parameters of **1-3** complexes.[a)]

Complex	Bond lengths [Å]					Bond angles [deg]		Dihedral angles [deg] [b)]				
	Pt-N^3	Pt-N^4	Pt-Cl	Pt-S	Pt-O	N-Pt-N	X-Pt-Y	N-Pt-S-O	H^t-N^3-Pt-Cl	H^c-N^3-Pt-Cl	H^t-N^4-Pt-Cl	H^c-N^4-Pt-Cl
1	2.035	2.052	2.306 [c)] 2.298 [d)]	-	-	83.91	93.12	-	41.65	-78.32	110.37	-129.60
2a’	2.108	2.100	2.346	2.296	-	82.15	93.03	-2.94	-149.68	95.15	-71.71	44.37
2b’	2.107	2.101	2.348	2.295	-	82.24	92.91	-3.42	42.94	-72.16	96.56	-147.44
3a	2.118	2.032	2.332	-	2.138	82.91	85.91	-	-128.95	113.37	-72.21	43.68
3b	2.037	2.111	2.334	-	2.135	82.91	85.76	-	42.43	-72.51	119.32	-121.88

[a)] **2a’** and **2b’** denotes position of DMSO-h_6 *trans* to N^4 and *trans* to N^3, respectively; **3a** and **3b** denotes position of H_2O *trans* to N^4 and *trans* to N^3, respectively

[b)] Stereochemical designations of protons attached to nitrogen atoms (N**H**) are based on the dihedral angles between a given NH bond and the adjacent CH bond (H-N-C-H); the smaller dihedral angle is assigned to *cisoid* arrangement while the larger dihedral angle to *transoid* arrangement, denoted as superscripts ^{c} and ^{t} , respectively

[c)] Cl *trans* to N^4

[d)] Cl *trans* to N^3