Supporting Information

Table S1 The optimized ground-state geometries of complex **1** obtained by different methods

	B3LYP	PEB0	M062X
Bond length (Å)			
Pt-N1	2.018	1.998	2.022
Pt-C1	1.916	1.902	1.901
Pt-N2	2.075	2.047	2.085
Pt-O1	2.085	2.064	2.103
Bond angle (º)			
C1-Pt-N2	79.96	80.25	80.05
C1-Pt-N1	82.75	82.79	82.72
N1-Pt-O1	94.51	95.15	94.07
N2-Pt-O1	102.76	101.79	103.14
C1-Pt-O1	176.65	177.17	175.85
Dihedral angle (º)			
N2-Pt-N1-C1	0.549	0.819	-0.837
O1-N1-C1-N2	1.205	1.147	-1.624

Table S2 Selected optimized geometric parameters of the ground-state and the lowest-lying triplet excited state for **1** at the different level

	B3LYP	B3LYP(PCM)	TD-B3LYP	TD-B3LYP(PCM)	B3LYP
	S_0	S_0	T_1	T_1	T_1
			Bond lengths (Å)		
Pt-N1	2.018	2.027(0.009)	2.012	2.012(0.000)	2.006(0.006）
Pt-C1	1.916	1.919(0.003)	1.918	1.920(0.002)	1.919(0.001)
Pt-N2	2.075	2.083(0.008)	2.077	2.091(0.014)	2.082(0.005)
Pt-O1	2.085	2.106(0.021)	2.195	2.161(0.034)	2.130(0.065)
			Bond angles (º)		
C1-Pt-N2	79.96	79.85(0.11)	80.21	80.03(0.18)	80.19(0.02)
C1-Pt-N1	82.75	82.58(0.17)	82.78	82.87(0.09)	83.02(0.24)
N1-Pt-O1	94.51	93.85(0.3)	91.16	91.20(0.04)	91.93(0.77)
N2-Pt-O1	102.76	103.71(0.95)	105.85	105.96(0.11)	104.87(0.98)
C1-Pt-O1	176.65	175.71(0.94)	173.49	173.68(0.19)	174.78(1.29)
			Dihedral angle (º)		
N2-Pt-N1-C1	0.549	-0.002(0.551)	-1.815	-2.940(1.125)	-1.648(0.167)
O1-N1-C1-N2	1.205	1.667(0.462)	2.182	2.310(0.128)	1.324(0.858)

Table S3 Molecular orbital compositions in the ground state for **1** at the DFT/B3LYP level

MO	Energy (eV)	Contribution (%)							Assign
		Pt	O	ph-a	ph-b	ph-c	py-a	py-b	
L+4	-0.218	4p		18	14	39			π^*(ph-a+ph-b+ph-c)
L+3	-0.898						69		π^*(py-a)
L+2	-1.333				18		11	41	π^*(ph-b+py-a+py-b)
L+1	-1.769			24				45	π^*(ph-a+py-b)
L	-1.796	3d/4p		15			54		π^*(ph-a+py-a)
H	-5.116	10d	23		47				d(Pt)+p(O)+π(ph-b)
H-1	-5.769	21d		38	13			15	d(Pt)+π(ph-a+ph-b+py-b)
H-2	-6.150	33d		20				16	d(Pt)+π(ph-a+py-b)
H-3	-6.313	12d		10	38				d(Pt)+π(ph-a+ph-b)
H-4	-6.340	71d/21s							d(Pt)+s(Pt)
H-5	-6.476	25d	31	9					d(Pt)+p(O)
H-6	-6.531		4			79			π(ph-c)
H-7	-6.640	5d		10	20	41			π(ph-a+ph-b+ph-c)

Table S4 Molecular orbital compositions in the ground state for **2** at the DFT/B3LYP level

MO	Energy (eV)	Contribution (%)							Assign
		Pt	O	ph-a	ph-b	ph-c	py-a	py-b	
L+4	-0.218	4p		13	13	45			π^*(ph-a+ph-b+ph-c)
L+3	-0.899						69		π^*(py-a)
L+2	-1.306				11		18	44	π^*(ph-b+py-a+py-b)
L+1	-1.769			31			9	39	π^*(ph-a+py-b)
L	-1.796	3d/4p		7			48	15	π^*(py-a+py-b)
H	-5.089	11d	22		44				d(Pt)+p(O)+π(ph-b)
H-1	-5.687	19d		38	16			13	d(Pt)+π(ph-a+ph-b+py-b)
H-2	-6.123	28d		27				17	d(Pt)+π(ph-a+py-b)
H-3	-6.286	14d		9	38			11	d(Pt)+π(ph-b+py-b)
H-4	-6.340	73d/21s							d(Pt)+s(Pt)
H-5	-6.449	28d	34						d(Pt)+p(O)
H-6	-6.504					84			π(ph-c)
H-7	-6.612	4d		10	21	42			π(ph-a+ph-b+ph-c)

Table S5 Molecular orbital compositions in the ground state for **3** at the DFT/B3LYP level

MO	Energy (eV)	Contribution (%)							Assign
		Pt	O	ph-a	ph-b	ph-c	py-a	py-b	
L+4	-0.190					78			π^*(ph-c)
L+3	-0.706						64		π^*(py-a)
L+2	-1.252				17		10	40	π^*(ph-b+py-a+py-b)
L+1	-1.660			26			45		π^*(ph-a+py-a)
L	-1.769	3p		9				54	π^*(py-b)
H	-5.116	11d	23		46				d(Pt)+p(O)+π(ph-b)
H-1	-5.714	20d		35	15			12	d(Pt)+π(ph-a+ph-b+py-b)
H-2	-6.068	16d		35			15	11	d(Pt)+π(ph-a+py-a+py-b)
H-3	-6.231	26d	5		20			11	d(Pt)+π(ph-b+py-b)
H-4	-6.286	73d/21s							d(Pt)+s(Pt)
H-5	-6.395	29d	32						d(Pt)+p(O)
H-6	-6.504					86			π(ph-c)
H-7	-6.558	5d		8	35	25			π(ph-b+ph-c)

Table S6 Molecular orbital compositions (%) in the first triplet excited state for three complexes **1-3** at the TD-DFT/B3LYP level

	MO	Energy (ev)	Contribution (%)							Assign
			Pt	O	ph-a	ph-b	ph-c	py-a	py-b	
1	L+1	-1.85			27			53		π^*(ph-a+py-a)
	H	-4.87	3	22		60				p(O)+π(ph-b)
2	L+1	-1.82			27			53		π^*(ph-a+py-a)
	H	-4.87	4	22		59				p(O)+π(ph-b)
3	L+1	-1.69			28			47		π^*(ph-a,py-a)
	L	-2.07					15		54	π^*(ph-c+py-b)
	H	-4.84	4	22		60				p(O)+π(ph-b)
	H-1	-5.74	28		40					d(Pt)+π(ph-a)

H-2	-6.07	31	17	15	d(Pt)+π(ph-a+py-b)