Organoplatinum chemistry related to alkane oxidation: The effect of a nitro substituent in ligands having an appended phenol group

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Supporting Material

***Table S1*. Summary of Crystal Data for complex 1**

Formula	$C_{15}H_{19}IN_2OPt$
Formula Weight (*g/mol*)	565.31
Crystal Dimensions (*mm*)	0.110 × 0.085 × 0.020
Crystal Color and Habit	colourless rectangular
Crystal System	orthorhombic
Space Group	P b c a
Temperature, K	110
a, Å	7.856(5)
b, Å	16.549(12)
c, Å	24.955(16)
α,°	90
β,°	90
γ,°	90
V, $Å^3$	3244(4)
Number of reflections to determine final unit cell	9976
Min and Max 2θ for cell determination, °	5.18, 57.34
Z	8
F(000)	2096
ρ (*g/cm*)	2.315
λ, Å, (MoKα)	0.71073
μ, (cm^{-1})	10.550
Diffractometer Type	Bruker Kappa Axis Apex2

Scan Type(s)	phi and omega scans
Max 2θ for data collection, °	57.472
Measured fraction of data	0.985
Number of reflections measured	48321
Unique reflections measured	4136
R_{merge}	0.1046
Number of reflections included in refinement	4136
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	$w=1/[sigma^2(Fo^2)+(0.0069P)^2+14.7589P]$ where $P=(Fo^2+2Fc^2)/3$
Number of parameters in least-squares	185
R_1	0.0348
wR_2	0.0447
R_1 (all data)	0.0671
wR_2 (all data)	0.0511
GOF	1.016
Maximum shift/error	0.002
Min & Max peak heights on final ΔF Map (e^-/Å)	-1.269, 1.180

Where:

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$

$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{½}$

$GOF = [\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns.} - \text{No. of params.})]^{½}$

***Table S2*. Summary of Crystal Data for complex 2**

Formula	$C_{29.50}H_{39.50}BrCl_{1.50}N_2OPt$
Formula Weight (*g/mol*)	766.30
Crystal Dimensions (*mm*)	0.212 × 0.122 × 0.034
Crystal Color and Habit	yellow plate
Crystal System	monoclinic
Space Group	P 2_1/c
Temperature, K	110
a, Å	17.567(7)
b, Å	18.400(8)
c, Å	19.284(8)
α,°	90
β,°	107.256(7)
γ,°	90
V, Å^3	5952(4)
Number of reflections to determine final unit cell	9915
Min and Max 2θ for cell determination, °	5.52, 60.16
Z	8
F(000)	3016
ρ (*g/cm*)	1.710
λ, Å, (MoKα)	0.71073
μ, (*cm*$^{-1}$)	6.216
Diffractometer Type	Bruker Kappa Axis Apex2
Scan Type(s)	phi and omega scans
Max 2θ for data collection, °	64.126
Measured fraction of data	0.997
Number of reflections measured	122016
Unique reflections measured	20198
R_{merge}	0.0879
Number of reflections included in refinement	20198
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	$w=1/[sigma^2(Fo^2)+(0.0241P)^2]$ where $P=(Fo^2+2Fc^2)/3$
Number of parameters in least-squares	721

R_1	0.0405
wR_2	0.0626
R_1 (all data)	0.0900
wR_2 (all data)	0.0742
GOF	0.992
Maximum shift/error	0.001
Min & Max peak heights on final ΔF Map (e^-/Å)	-1.395, 1.392

Where:

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$

$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{½}$

GOF = $[\Sigma(w(F_o^2 - F_c^2)^2) / (\text{No. of reflns. - No. of params.})]^{½}$

***Table S3*. Summary of Crystal Data for Complex 5**

Formula	$C_{23}H_{27}N_3O_5Pt$
Formula Weight (*g/mol*)	620.56
Crystal Dimensions (*mm*)	0.129 × 0.077 × 0.071
Crystal Color and Habit	yellow prism
Crystal System	monoclinic
Space Group	P 2_1/n
Temperature, K	110
a, Å	12.569(5)
b, Å	13.718(6)
c, Å	13.791(6)
α,°	90
β,°	110.79(2)
γ,°	90
V, $Å^3$	2223.1(16)
Number of reflections to determine final unit cell	9889
Min and Max 2θ for cell determination, °	5.46, 68.56
Z	4
F(000)	1216
ρ (*g/cm*)	1.854
λ, Å, (MoKα)	0.71073
μ, (cm^{-1})	6.352
Diffractometer Type	Bruker Kappa Axis Apex2
Scan Type(s)	phi and omega scans
Max 2θ for data collection, °	78.906
Measured fraction of data	0.999
Number of reflections measured	241379
Unique reflections measured	13302
R_{merge}	0.0849
Number of reflections included in refinement	13302
Cut off Threshold Expression	I > 2sigma(I)
Structure refined using	full matrix least-squares using F^2
Weighting Scheme	w=1/[sigma^2(Fo^2)+(0.0185P)^2+1.1302P] where P=(Fo^2+2Fc^2)/3
Number of parameters in least-squares	304

R_1	0.0246
wR_2	0.0473
R_1 (all data)	0.0396
wR_2 (all data)	0.0513
GOF	1.025
Maximum shift/error	0.006
Min & Max peak heights on final ΔF Map (e^-/Å)	-1.240, 1.062

Where:

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma F_o$

$wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w F_o^4)]^{½}$

GOF = [$\Sigma(w(F_o^2 - F_c^2)^2)$ / (No. of reflns. - No. of params.)]

Table S4. **Selected Bond Lengths and Angles for Complex 1**

Pt1-C1	2.047(5)	C1-Pt1-C2	87.2(2)
Pt1-C2	2.050(6)	C1-Pt1-C3	86.2(2)
Pt1-C3	2.060(5)	C2-Pt1-C3	88.4(2)
Pt1-N2	2.161(5)	C1-Pt1-N2	98.7(2)
Pt1-N1	2.164(5)	C2-Pt1-N2	173.5(2)
Pt1-I1	2.7803(14)	C3-Pt1-N2	89.5(2)
N1-C4	1.339(7)	C1-Pt1-N1	174.4(2)
		C2-Pt1-N1	97.2(2)
		C3-Pt1-N1	90.5(2)
		N2-Pt1-N1	76.69(18)
		C1-Pt1-I1	92.46(17)
		C2-Pt1-I1	90.20(17)
		C3-Pt1-I1	178.06(17)
		N2-Pt1-I1	92.10(12)
		N1-Pt1-I1	91.01(12)

***Table S5*. Selected Bond Lengths and Angles for complex 2**

Pt1-C2A	2.045(4)	C2A-Pt1-C1A	86.13(15)
Pt1-C1A	2.049(4)	C2A-Pt1-C3A	88.19(16)
Pt1-C3A	2.075(4)	C1A-Pt1-C3A	84.75(15)
Pt1-N1A	2.156(3)	C2A-Pt1-N1A	96.88(14)
Pt1-N2A	2.186(3)	C1A-Pt1-N1A	176.77(13)
Pt1-Br1A	2.6076(11)	C3A-Pt1-N1A	96.51(13)
		C2A-Pt1-N2A	172.31(14)
		C1A-Pt1-N2A	101.11(13)
		C3A-Pt1-N2A	89.89(13)
		N1A-Pt1-N2A	75.94(11)
		C2A-Pt1-Br1A	93.10(12)
		C1A-Pt1-Br1A	92.62(11)
		C3A-Pt1-Br1A	176.98(10)
		N1A-Pt1-Br1A	86.05(8)
		N2A-Pt1-Br1A	89.19(8)

***Table S6*. Selected Bond Lengths and Angles for Complex 5**

Pt1-O2	1.9936(15)	O2-Pt1-C6	90.27(6)
Pt1-C6	1.9968(18)	O2-Pt1-O1	176.25(5)
Pt1-O1	2.0447(15)	C6-Pt1-O1	89.95(6)
Pt1-C1	2.0500(18)	O2-Pt1-C1	89.91(7)
Pt1-N1	2.1567(16)	C6-Pt1-C1	81.24(7)
Pt1-N2	2.1725(16)	O1-Pt1-C1	93.82(7)
		O2-Pt1-N1	90.58(6)
		C6-Pt1-N1	177.58(6)
		O1-Pt1-N1	89.05(6)
		C1-Pt1-N1	101.02(7)
		O2-Pt1-N2	93.88(6)
		C6-Pt1-N2	99.15(7)
		O1-Pt1-N2	82.39(6)
		C1-Pt1-N2	176.19(6)

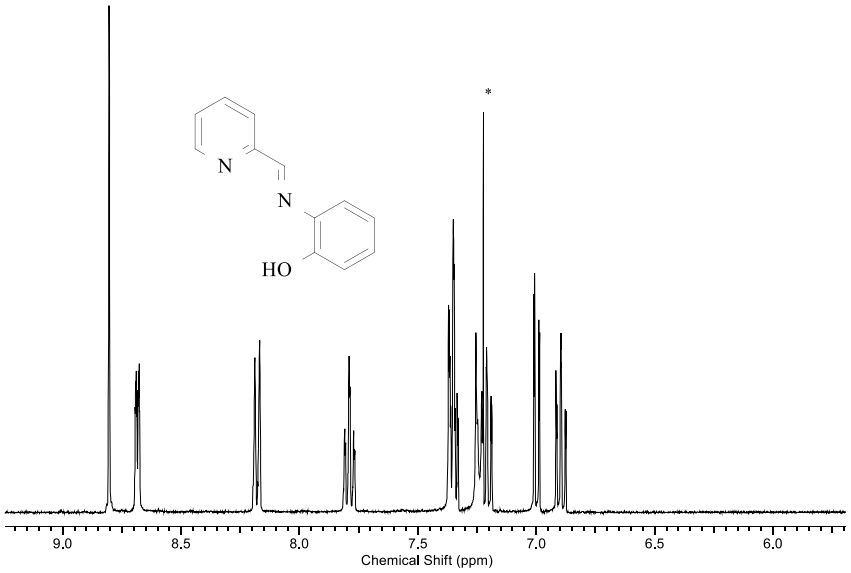

Figure S1. ^{1}H NMR spectrum of ligand **L2**.

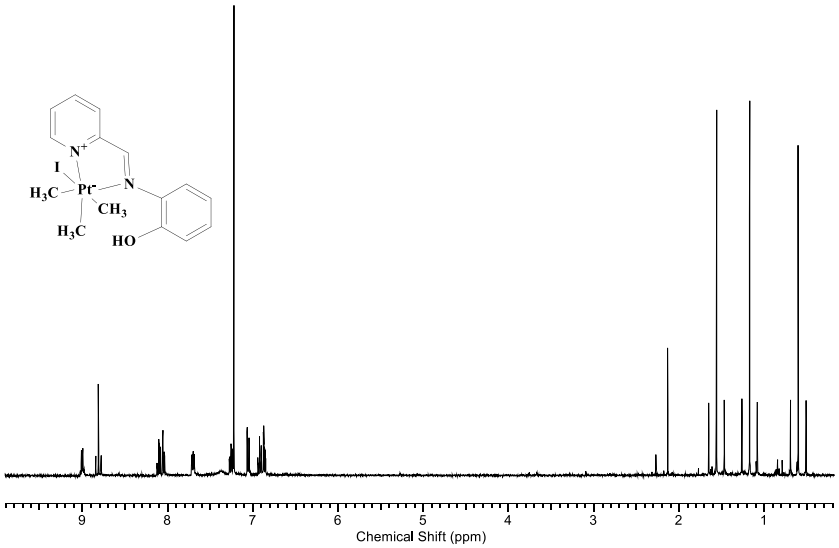

Figure S2. ^{1}H NMR spectrum of complex **1**.

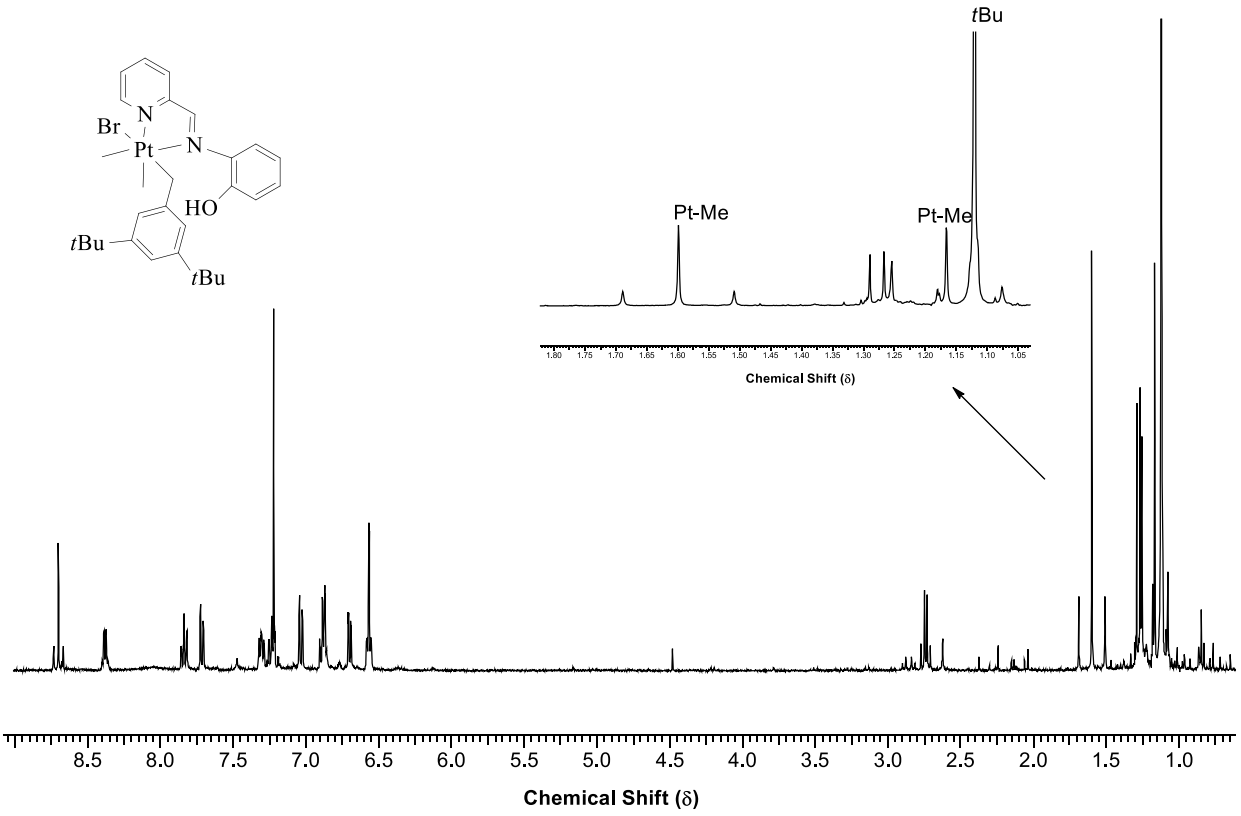

Figure S3. ^{1}H NMR spectrum of complex **2**.

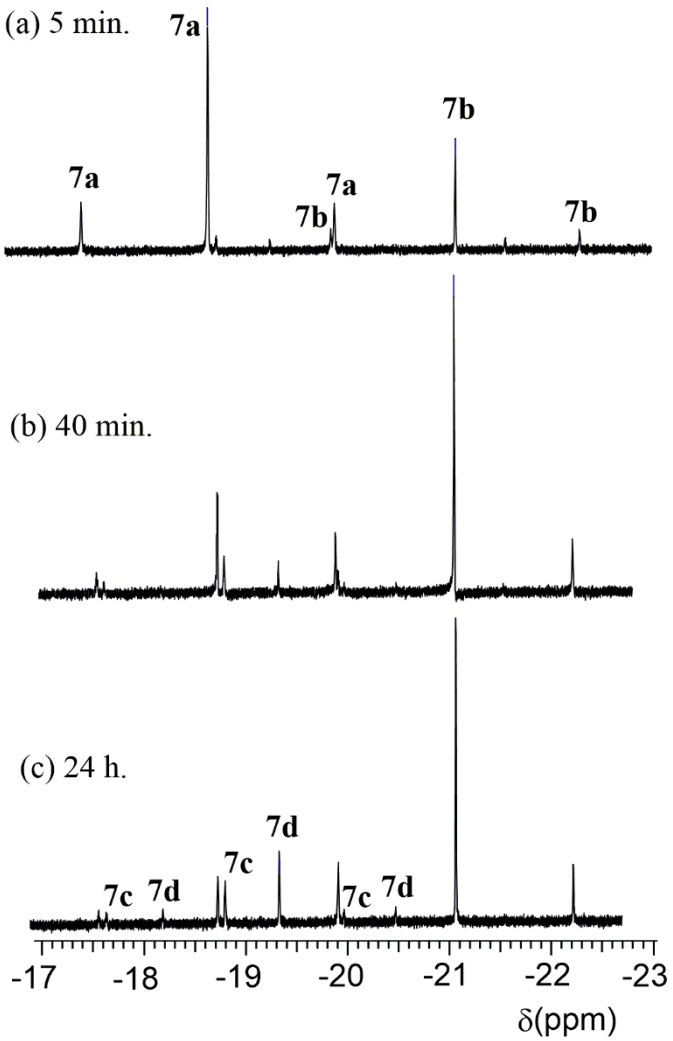

Figure S4. ^{1}H NMR spectra in the PtH region during formation and isomerization of complexes **7a-7d**.