Supporting Information

Synthesis and characterization of new Pd(II) and Pt(II) complexes with 3-substituted 1-(2-pyridyl)imidazo[1,5-*a*]pyridine ligands.

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Supporting Information

1. NMR data

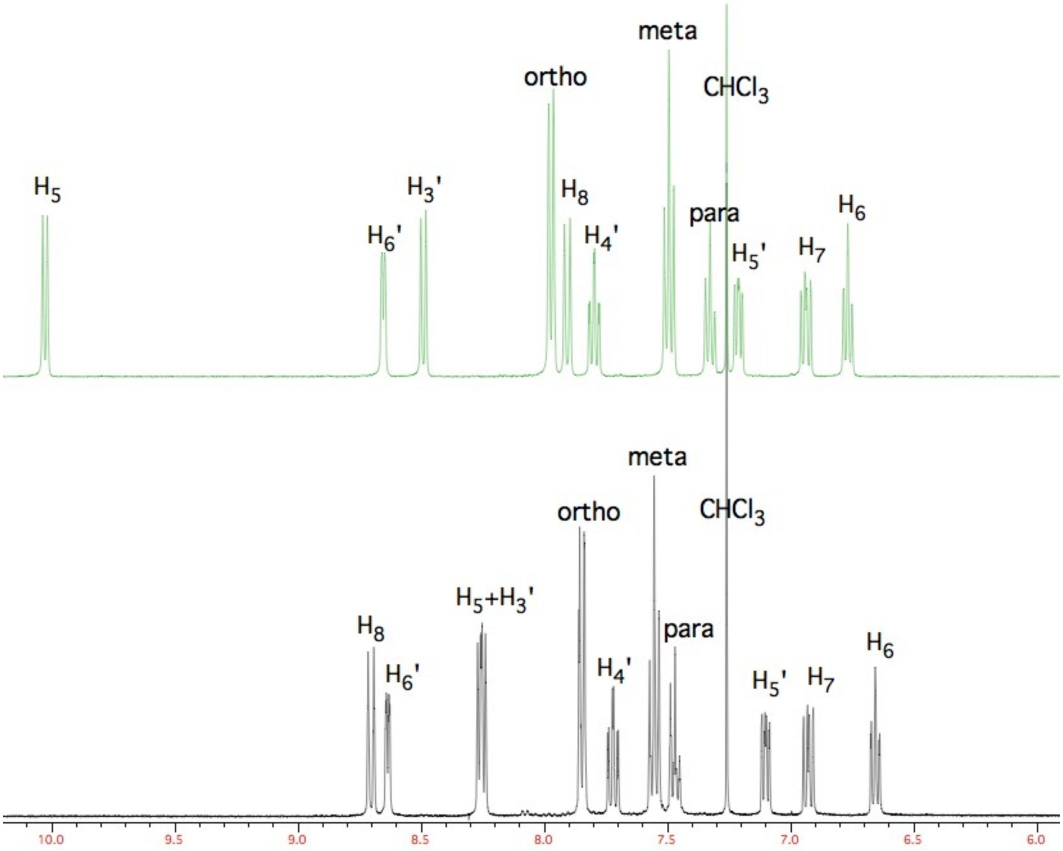
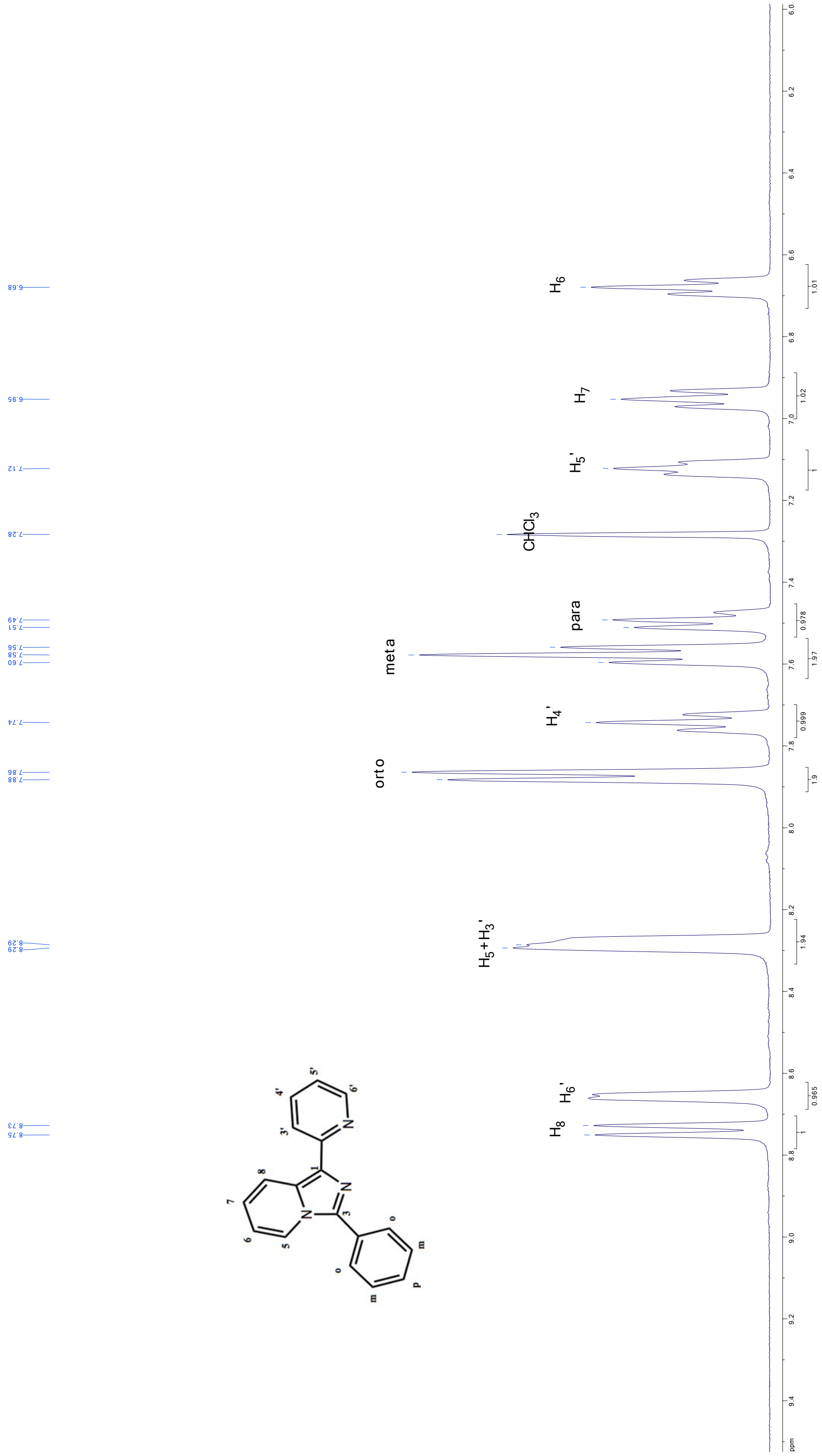
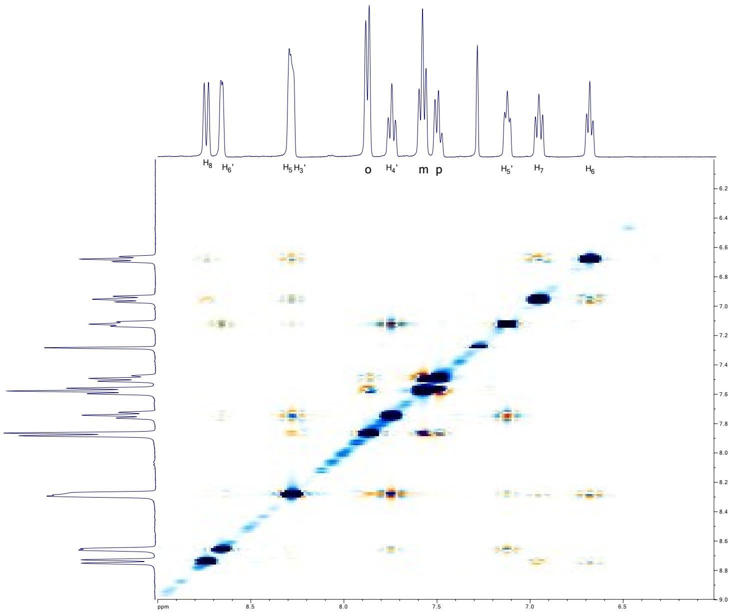


Figure S1. ^{1}H NMR spectra of L^1 (down) and L^1 isomer (upper)

^{1}H NMR spectrum of L^1 in CDCl$_3$

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H6'
H5 H3'
o
H4'
m p
H5'
H7
H6
ppm
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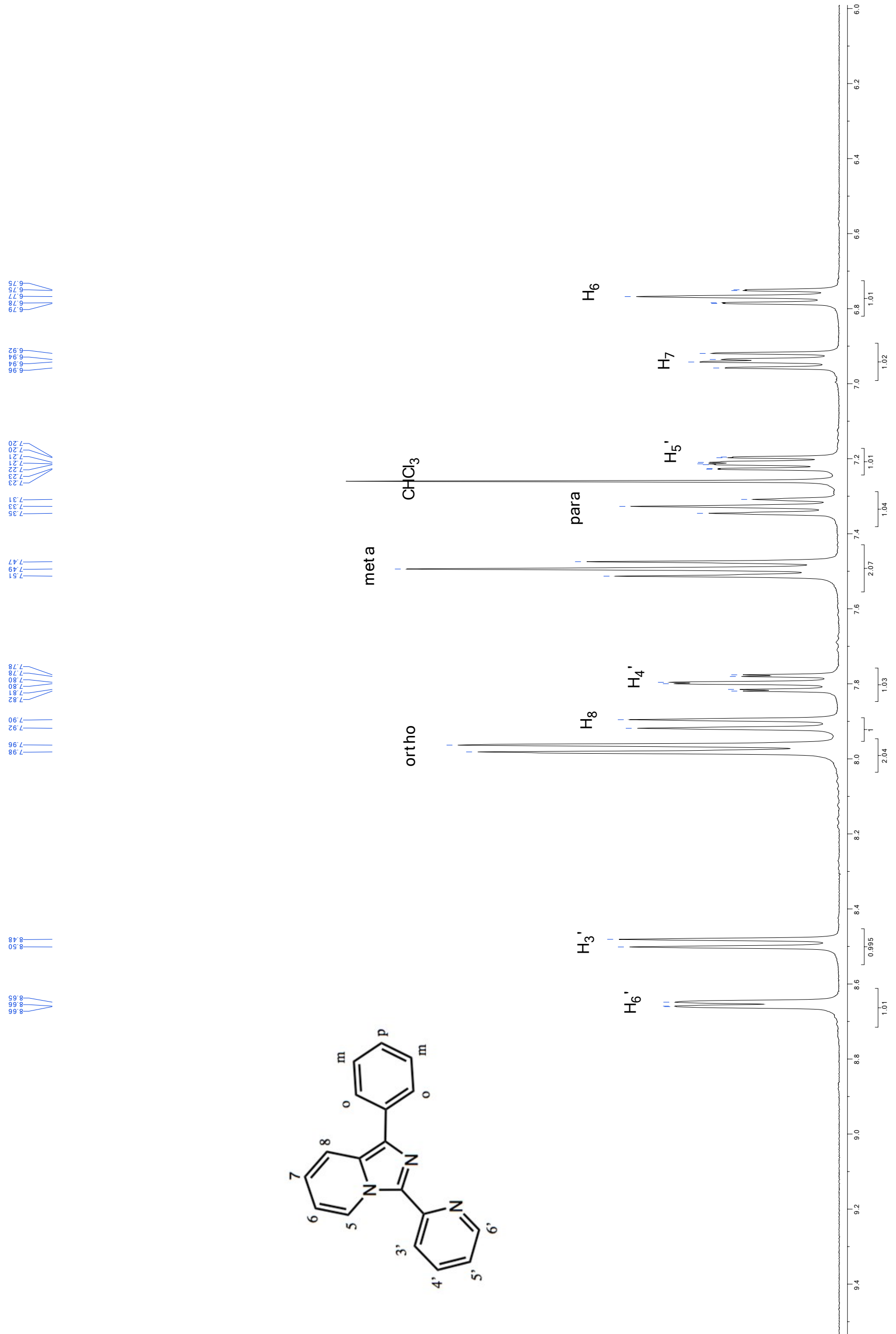
7.0
6.5
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0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H7
H5'
CHCl3
para
meta
H4'
H8
ortho
H3'
H6'
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1.02
1.01
1.04
2.07
1.03
1
2.04
0.995
1.01
6.0
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
o
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p
m
o
8
7
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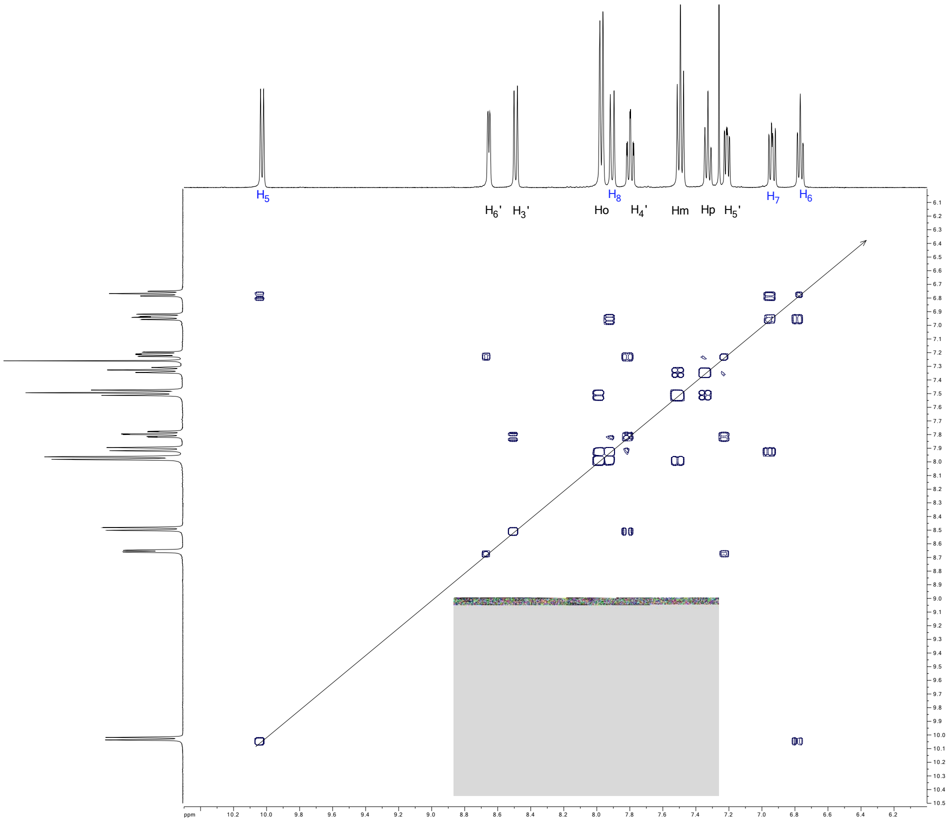
5
N
N
N
3'
4'
5'
6'

Supporting Information

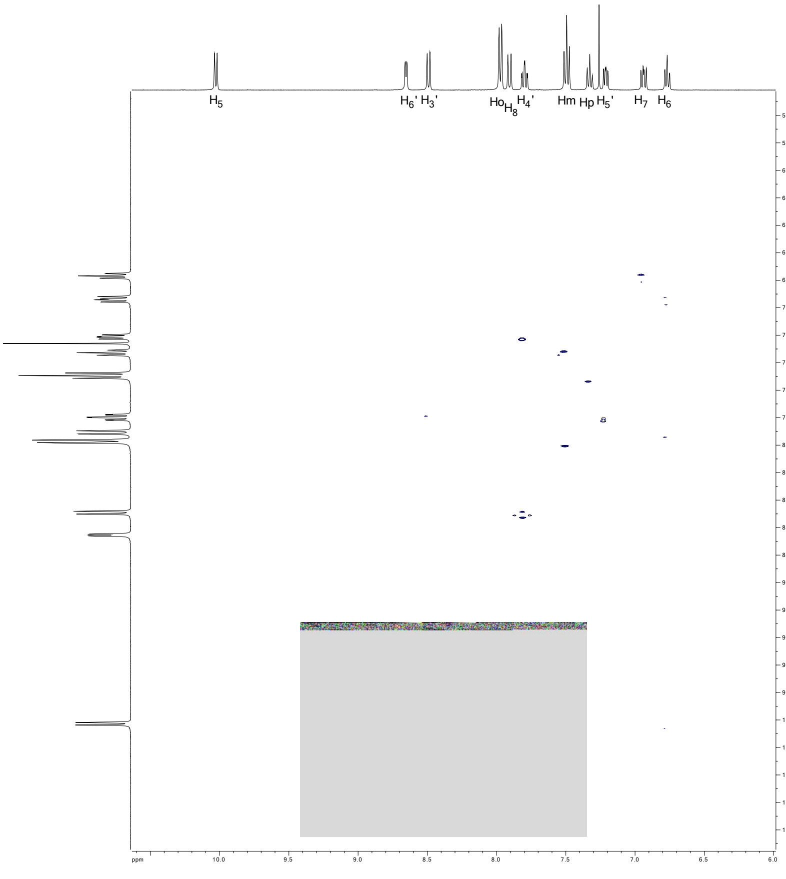


^{1}H-^{1}H COSY NMR spectrum of L^1 in $CDCl_3$

^{1}H-^{1}H NOESY NMR spectrum of L^1 isomer in $CDCl_3$

2. Crystallography

Crystallographic Method



The crystal data for **5**, **8**, **10**, **11** and **14** are compiled in Tables S1-S4. Crystals of **5** were examined with an Xcalibur Gemini diffractometer, equipped with a Ruby CCD area detector and mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystals of **10** were examined using an Agilent Supernova diffractometer, equipped with CCD area detector and mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystals of **14** were examined with an Xcalibur Oxford Diffraction diffractometer, equipped with CCD area detector and mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystals of **8** and **11** were examined with a Rigaku XtalLAB AFC11 diffractometer equipped with a CCD area detector and graphite-monochromated Cu Kα (λ = 1.54178 Å) or Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on 1° frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed or multi-scan absorption correction with a beam profile was applied.[1] The structures were solved using SHELXS or SHELXT;[2] the datasets were refined by full-matrix least-squares on all unique F^2 values,[3] with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; U_{iso}(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. CrysAlisPro[1] was used for control and integration, and SHELX[2,3] was employed through OLEX2[4] for structure solution and refinement, which was also used for molecular graphics. CCDC 2061441-2061445 contain the supplementary crystal data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Structural characterisation

The solid state X-ray structures of all heteroleptic complexes analysed in this study (**10**, **11** and **14**) all present minor components in which the two anionic ligands (methyl and chloride) are swapped. The positional disorder was clearly identified in each case and successfully modelled by refining the occupancies competitively. The models obtained for **10**, **11** and **14** are in good agreement with the spectroscopic data, wherein the isomers **10'**, **11'** and **14'** are present as minor components (15%, 5% and 15% respectively). Owing to the low occupancies of the minor isomers and large statistical uncertainty of their metric parameters, a rigorous comparison cannot be drawn with the main components.

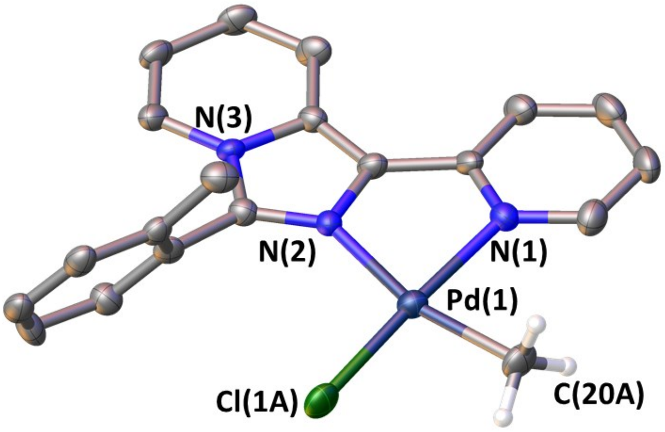


Figure S2: Molecular structure of **10’** with ellipsoids set at 50% probability level. Hydrogens have been omitted for clarity with the exception of those belonging to methyl group C(20A).

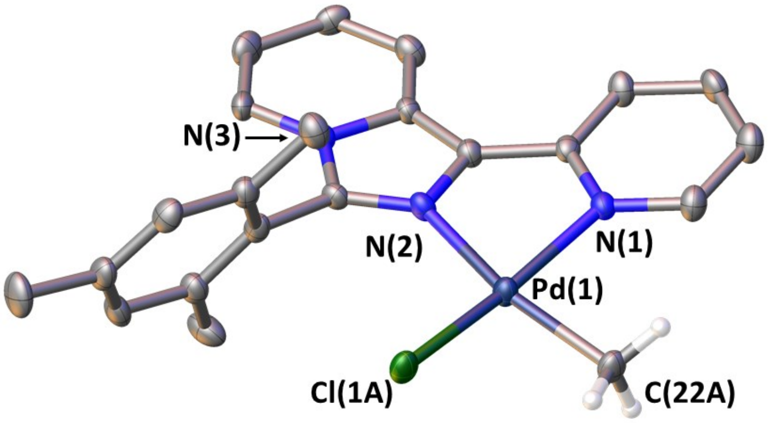


Figure S3: Molecular structure of **11’** with ellipsoids set at 50% probability level. Hydrogens have been omitted for clarity with the exception of those belonging to methyl group C(20A).

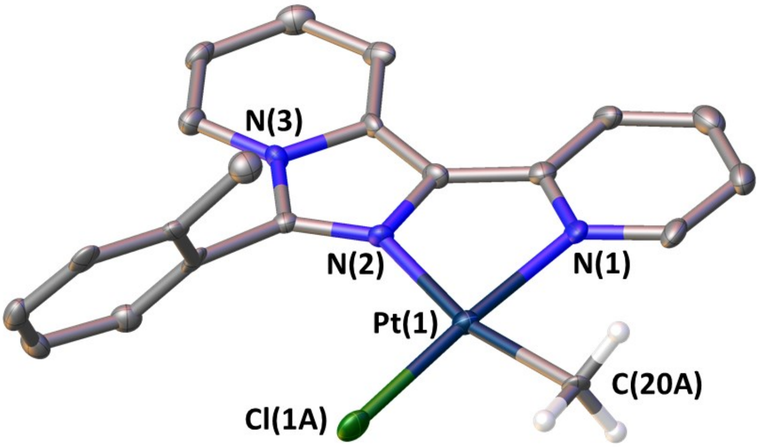


Figure S4: Molecular structure of **14’** with ellipsoids set at 50% probability level. Hydrogens have been omitted for clarity with the exception of those belonging to methyl group C(20A).

Table S1. Selected bond lengths (Å) and angles (º) for **10**, **11** and **14**

	10	**11**	**14**
M−N1	2.147(4)	2.148(3)	2.110(4)
M−N2	2.068(4)	2.055(3)	2.026(4)
M−Cl1	2.300(2)	2.3064(12)	2.285(2)
M−CH_3	2.069(9)	2.049(5)	2.07(1)
N1−M−N2	79.67(15)	78.94(12)	79.5(2)
N1−M−Cl1	94.97(12)	95.32(9)	94.54(14)
N2−M−Cl1	174.64(13)	173.01(9)	173.96(14)
N1−M−CH_3	172.5(3)	175.3(2)	173.9(4)
N2−M−CH_3	94.2(3)	96.44(12)	95.7(3)
Cl1−M−CH_3	91.1(2)	89.22(14)	90.3(3)

Table S2. Selected bond lengths (Å) and angles (º) for **5** and **8**

	5	**8**
M−N1	2.020(2)	2.028(3)
M−N2	2.023(2)	2.029(3)
M−Cl1	2.2896(8)	2.2883(8)
M−Cl2	2.2869(8)	2.2961(10)
M−CH_3	-	-
N1−M−N2	80.60(9)	80.44(11)
N1−M−Cl1	94.19(7)	94.25(9)
N1−M−Cl2	177.23(7)	178.42(8)
Cl1−M−Cl2	87.69(3)	87.31(3)
N2−M−Cl1	174.63(7)	174.60(7)
N2−M−Cl2	94.47(7)	98.00(7)

Table S3: Crystallographic parameters for **5**, **8**, and **10**.

[a]Conventional $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $Rw = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; $S = [\Sigma w(Fo^2 - Fc^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

	5	**8**	**10**
Formula	$C_{18}H_{13}Cl_2N_3Pt$	$C_{19}H_{15}Cl_2N_3Pt$	$C_{20}H_{18}ClN_3Pd$
FW	537.30	551.33	442.22
cryst size, mm	0.04 x 0.10 x 0.25	0.05 x 0.10 x 0.10	0.07 x 0.12 x 0.14
crystal syst	monoclinic	monoclininc	Orthorombic
space group	$P2_1$/n	$P2_1/c$	$P2_1$/c
a, Å	7.48068(13)	7.2451(1)	6.7186(5)
b, Å	18.9967(3)	11.8636(1)	18.0115(11)
c, Å	11.6695(2)	20.2553(2)	14.8207(10)
α, °	90	90	90
β, °	103.136(2)	99.331(1)	101.194(7)
γ, °	90	90	90
V, Å^3	1614.94(5)	1717.97(3)	1759.4(2)
Z	4	4	4
ρ_{calcd}, g cm^3	2.102	2.132	1.669
μ, mm^{-1}	9.023	18.188	1.214
F(*000*)	1016	1048	888
no. of reflections (unique)	21290 (4607)	9235 (3102)	6580 (3859)
S^a	1.04	1.05	1.04
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0227(0.0464)	0.0243(0.0663)	0.0541(0.1027)
R_{int}	0.039	0.030	0.047
min., max. diff map, e Å^{-3}	–0.85, 1.00	–1.19, 0.98	–0.89. 0.59

Table S4: Crystallographic parameters for **11** and **14.**

[a]Conventional $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $Rw = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; $S = [\Sigma w(Fo^2 - Fc^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

	11	**14**
Formula	$C_{22}H_{22}ClN_3Pd$	$C_{20}H_{18}ClN_3Pt$
FW	470.27	530.91
cryst size, mm	0.06 x 0.08 x 0.11	0.19 x 0.23 x 0.36
crystal syst	triclinic	monoclininc
space group	*P*-1	$P2_1/c$
a, Å	8.6794(7)	6.6611(3)
b, Å	10.7831(9)	17.9170(7)
c, Å	10.8932(9)	14.6855(6)
α, °	73.015(8)	90
β, °	80.802(7)	101.376(4)
γ, °	85.043(7)	90
V, Å^3	961.65(14)	1718.24(13)
Z	2	4
ρ_{calcd}, g cm^3	1.624	2.052
μ, mm^{-1}	1.115	8.329
F(*000*)	476	1016
no. of reflections (unique)	10385 (4473)	8191 (3119)
S^a	1.03	1.03
$R_1(wR_2)$ ($F^2 > 2\sigma(F^2)$)	0.0434(0.0926)	0.0318(0.0586)
R_{int}	0.050	0.040
min., max. diff map, e Å^{-3}	–0.65, 0.59	–1.30, 1.24

3. Computational Details

Table S5. Selected bond lengths, angles and dihedral for the complexes [Pt(L^1)Cl$_2$], [Pt(L^2)Cl$_2$] and [Pt(L^4)Cl$_2$].

	[Pt(L^1)Cl$_2$]		**[Pt(L^2)Cl$_2$]**		**[Pt(L^4)Cl$_2$]**	
Parameter [a]	Exptl.[b]	Calcd.	Exptl.[b]	Calcd.	Exptl.[b]	Calcd.
Pt(II)-N(1)	2.023	2.070	2.026	2.056	2.029	2.069
Pt (II)-N(2)	2.020	2.072	2.110	2.074	2.028	2.068
Pt (II)-Cl(1)	2.290	2.317	2.285	2.319	2.288	2.319
Pt (II)-Cl(2)	2.287	2.320	2.217	2.319	2.296	2.327
N(1)-Pt(II)-N(2)	80.60	79.19	79.48	79.29	80.44	79.17
N(1)-Pt(II)-Cl(2)	97.47	98.03	101.87	97.17	98.00	98.89
N(2)-Pt(II)-Cl(1)	94.19	93.84	95.54	94.09	94.24	93.83
Cl(1)-Pt(II)-Cl(2)	87.69	88.88	84.05	89.45	87.31	88.11
N(1)–X(α)–X(β)–X(γ)	66.99	58.45	63.68	83.04	96.126	107.53
X(α)–X(β)–X(γ)	--	--	--	--	113.57	112.94
X(α)–X(β)–X(γ)–X(δ)	--	--	--	--	132.60	122.08

[a] Distances in Å and angles in degrees. [b] structural data from this work.

4. References

1. *CrysAlisPRO*, version 39.27b; Oxford Diffraction /Agilent Technologies UK Ltd: Yarnton, U.K., 2017
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*., 2008, **64**, 112.
3. G. M. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339.