Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Substituent effects in solution speciation of the mononuclear and dinuclear trimethylplatinum(IV) iodide complexes of pyridines

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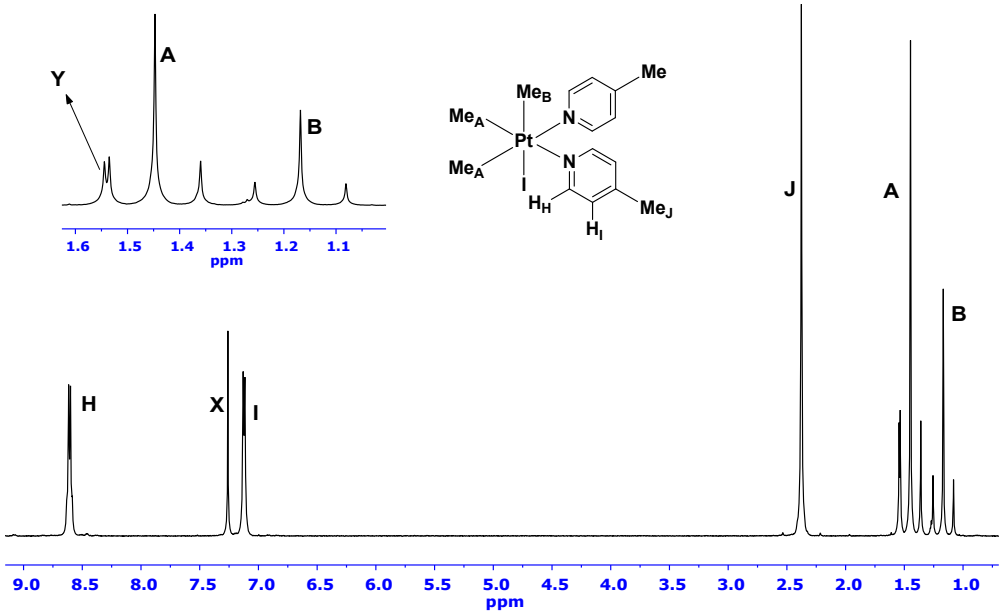
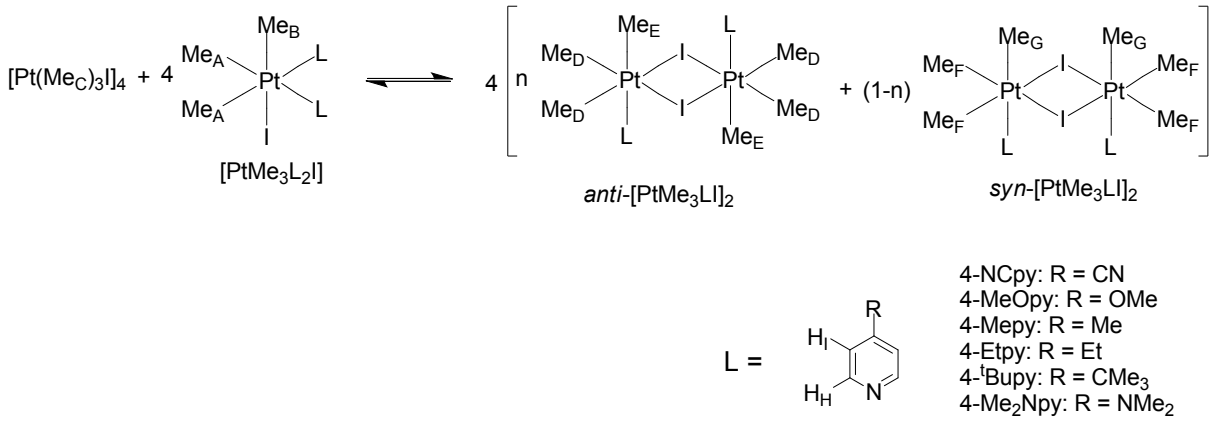


Fig.S1 The 400 MHz ^{1}H NMR spectrum of mononuclear [$PtMe_3(4\text{-}Mepy)_2I$] in $CDCl_3$. X is the solvent peak and Y is the peak for water molecules present in $CDCl_3$. Inset showing the signals for the methyl groups bonded to platinum metal.



L =

4-NCpy: R = CN
4-MeOpy: R = OMe
4-Mepy: R = Me
4-Etpy: R = Et
4-^{t}Bupy: R = CMe_3
4-Me_2Npy: R = NMe_2

Scheme S1 The reaction of tetrameric trimethylplatinum(IV) iodide and mononuclear $[PtMe_3L_2I]$ (L = pyridines) complexes in chloroform showing the labelling.

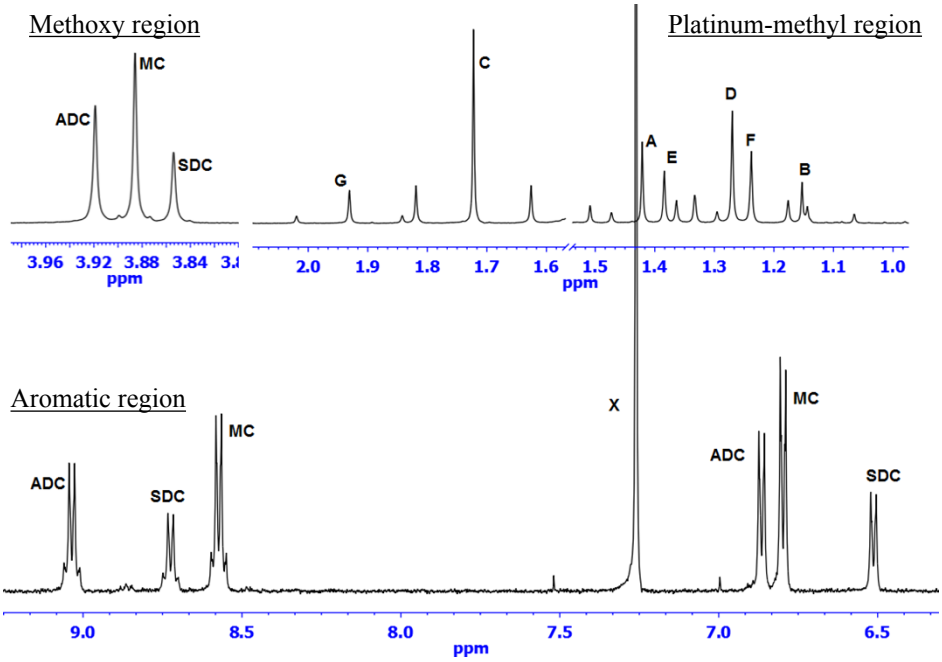


Fig. S2 400 MHz ^1H NMR spectrum of 1:1 mixture of $[PtMe_3(4\text{-}MeOpy)_2I]$ and $[(PtMe_3I)_4]$ in $CDCl_3$, measured at room temperature. Here ADC = *anti*-$[PtMe_3(4\text{-}MeOpy)I]_2$, SDC = *syn*-$[PtMe_3(4\text{-}MeOpy)I]_2$ and MC = mononuclear $[PtMe_3(4\text{-}MeOpy)_2I]$. X is the solvent peak. Labelling in the platinum-methyl region refers to Scheme S1.

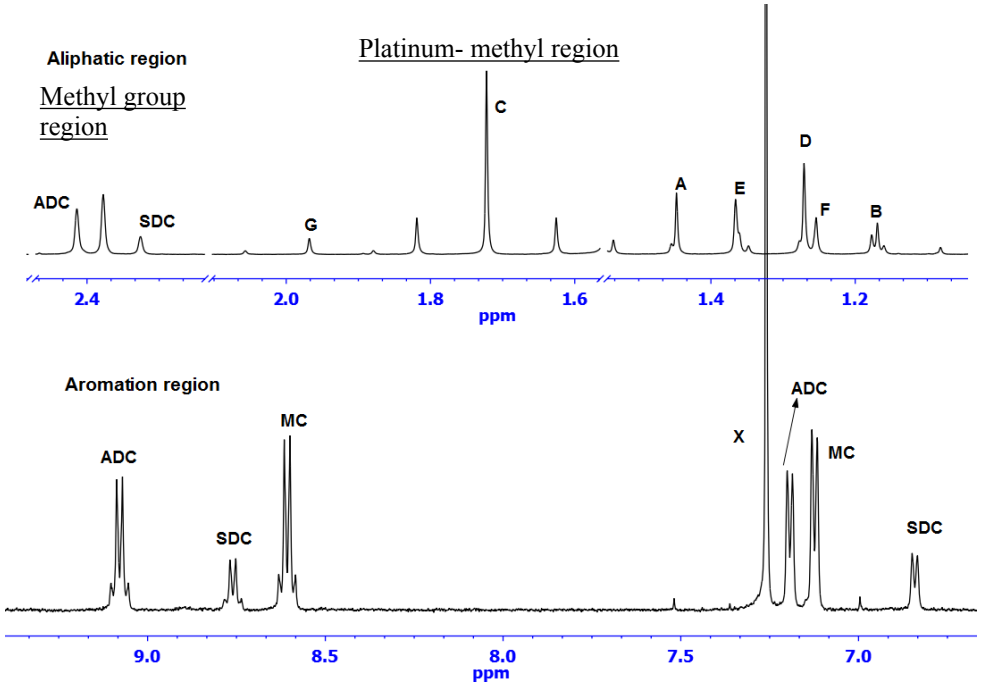


Fig. S3 400 MHz ^{1}H NMR spectrum of 1:1 mixture of [$PtMe_3(4\text{-}Mepy)_2I$] and [$(PtMe_3I)_4$] in $CDCl_3$, measured at room temperature. Here ADC = *anti*-[$PtMe_3(4\text{-}Mepy)I]_2$, SDC = *syn*-[$PtMe_3(4\text{-}Mepy)I]_2$ and MC = mononuclear [$PtMe_3(4\text{-}Mepy)_2I$]. X is the solvent peak. Labelling of methyl groups in the platinum-methyl region refers to scheme S1.

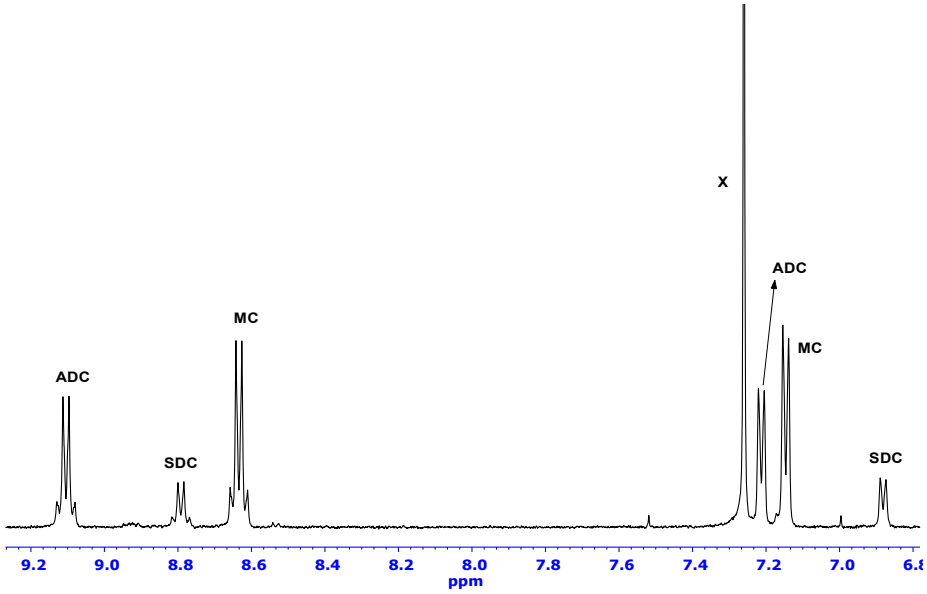


Fig. S4 Aromatic region in the 400 MHz ^{1}H NMR spectrum of 1:1 mixture of [$PtMe_3(4\text{-}Etpy)_2I$] and [$(PtMe_3I)_4$] in $CDCl_3$, measured at room temperature. Here ADC = *anti*-[$PtMe_3(4\text{-}Etpy)I]_2$, SDC = *syn*-[$PtMe_3(4\text{-}Etpy)I]_2$ and MC = mononuclear [$PtMe_3(4\text{-}Etpy)_2I$]. X is the solvent peak.

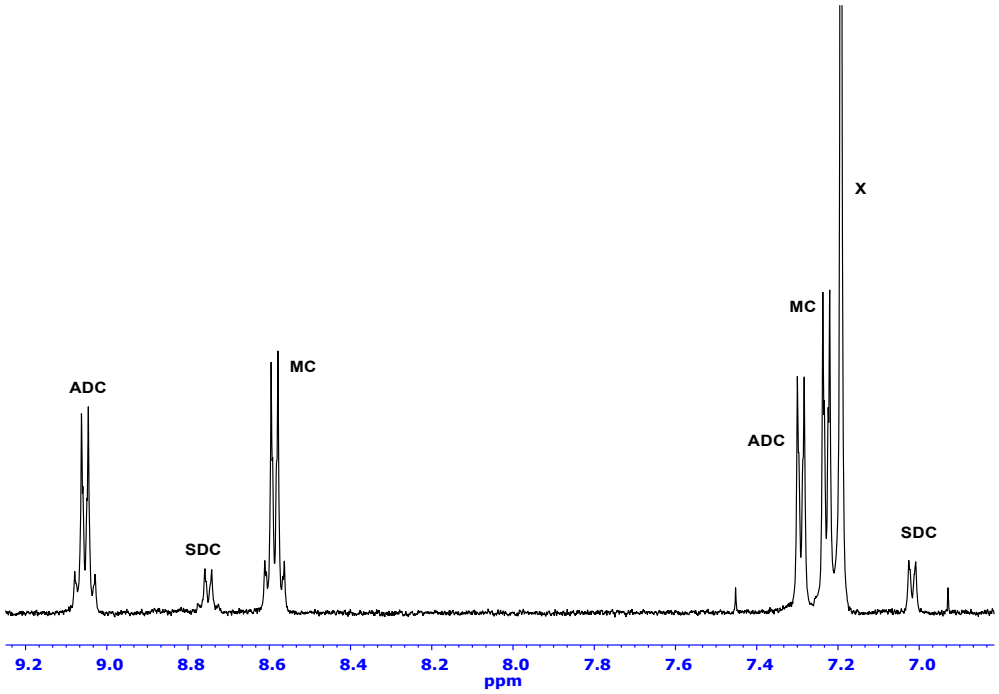


Fig. S5 Aromatic region in the 400 MHz ^{1}H NMR spectrum of 1:1 mixture of [$PtMe_3(4\text{-}^t\text{Bupy})_2I$] and [$(PtMe_3I)_4$] in $CDCl_3$, measured at room temperature. Here ADC = *anti*-[$PtMe_3(4\text{-}$

^{t}Bupy)I]$_2$, SDC = *syn*-[PtMe$_3$(4-^{t}Bupy)I]$_2$ and MC = mononuclear [PtMe$_3$(4-^{t}Bupy)$_2$I]. X is the solvent peak.

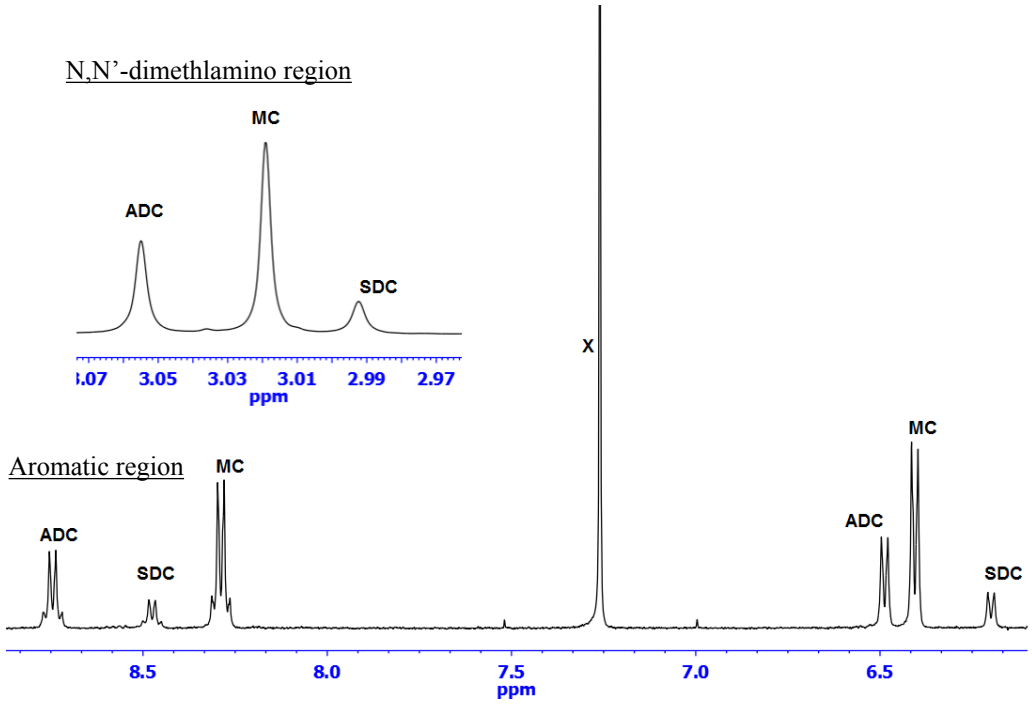


Fig. S6 400 MHz ^{1}H NMR spectrum of 1:1 mixture of [PtMe$_3$(4-Me$_2$Npy)$_2$I] and [(PtMe$_3$I)$_4$] in CDCl$_3$, measured at room temperature. Here ADC = *anti*-[PtMe$_3$(4-Me$_2$Npy)I]$_2$, SDC = *syn*-[PtMe$_3$(4-Me$_2$Npy)I]$_2$ and MC = mononuclear [PtMe$_3$(4-Me$_2$Npy)$_2$I]. X is the solvent peak.

Table S1 ^{1}H NMR data[a] for the reaction of trimethylplatinum(IV) iodide with mononuclear [$PtMe_3L_2I$] (L= pyridines) complexes in $CDCl_3$

$PtMe_3L_2I$ complex	Pt(IV) species present in solution	δ(Pt-Me)[b, e]	*Trans* ligand	δ(ligand H)[c, e]
[$PtMe_3$(4-NCpy)$_2$I][1]	[$PtMe_3$(4-NCpy)$_2$I]	A 1.53 (71.2) B 1.18 (67.3)	4-NCpy I	H 9.04 (6.4) (17.9) [d] I 7.64 (6.5)
	$PtMe_3I$	C 1.72 (77.3)	I	-
	anti-[$PtMe_3$(4-NCpy)I]$_2$	D 1.27 (73.9) E 1.41 (72.5)	I 4-NCpy	H 9.47 (6.4) (18.5) [d] I 7.67 (6.5)
	syn-[$PtMe_3$(4-NCpy)I]$_2$	F 1.25 G 2.04 (72.6)	I 4-NCpy	H 9.18 I 7.37
[$PtMe_3$(4-MeOpy)$_2$I]	[$PtMe_3$(4-MeOpy)$_2$I]	A 1.42 (70.0) B 1.15 (70.2)	4-MeOpy I	H 8.58 (7.0) (19.0) [d] I 6.80 (7.0) OMe 3.89
	$PtMe_3I$	C 1.72 (77.3)	I	-
	anti-[$PtMe_3$(4-MeOpy)I]$_2$	D 1.27 (75.1) E 1.38 (71.0)	I 4-MeOpy	H 9.04 (6.9) (19.7) [d] I 6.86 (7.0) OMe 3.92
	syn-[$PtMe_3$(4-MeOpy)I]$_2$	F 1.24 (75.2) G 1.93 (71.0)	I 4-MeOpy	H 8.73 (6.8) (19.5) [d] I 6.51 (6.9) OMe 3.85
[$PtMe_3$(4-Mepy)$_2$I][2]	[$PtMe_3$(4-Mepy)$_2$I]	A 1.45 (70.0) B 1.17 (70.0)	4-Mepy I	H 8.61 (6.4) (19.0) [d] I 7.12 (6.0) Me 2.38
	$PtMe_3I$	C 1.72 (77.3)	I	-
	anti-[$PtMe_3$(4-Mepy)I]$_2$	D 1.27 (75.1) E 1.37 (71.1)	I 4-Mepy	H 9.08 (6.5) (19.6) [d] I 7.19 (6.0) Me 2.41
	syn-[$PtMe_3$(4-Mepy)I]$_2$	F 1.25 (75.1) G 1.97 (71.1)	I 4-Mepy	H 8.76 (6.4) (19.2) [d] I 6.84 (5.8) Me 2.33
[$PtMe_3$(4-Etpy)$_2$I]	[$PtMe_3$(4-Etpy)$_2$I]	A 1.45 (70.1) B 1.18 (70.2)	4-Etpy I	H 8.64 (6.4) (18.9) [d] I 7.15 (6.4) CH_2 2.68 Me 1.27
	$PtMe_3I$	C 1.72 (77.3)	I	-
	anti-[$PtMe_3$(4-Etpy)I]$_2$	D 1.28 (75.1) E 1.36 (71.0)	I 4-Etpy	H 9.11 (6.6) (19.8) [d] I 7.21 (6.3) CH_2 2.72 Me 1.30
	syn-[$PtMe_3$(4-Etpy)I]$_2$	F 1.28 (75.1) G 1.99 (71.1)	I 4-Etpy	H 8.79 (6.5) (19.4) [d] I 6.88 (6.1) CH_2 2.62 Me 1.26
[$PtMe_3$(4-^{t}Bupy)$_2$I]	[$PtMe_3$(4-^{t}Bupy)$_2$I]	A 1.45 (69.9) B 1.19 (70.1)	4-^{t}Bupy I	H 8.66 (6.5) (19.0) [d] I 7.30 (6.7) ^{t}Bu 1.33
	$PtMe_3I$	C 1.72 (77.3)	I	-
	anti-[$PtMe_3$(4-^{t}Bupy)I]$_2$	D 1.30 (75.1) E 1.35 (70.8)	I 4-^{t}Bupy	H 9.12 (6.6) (19.8) [d] I 7.36 (6.6) ^{t}Bu 1.35

	syn-[$PtMe_3$(4-^{t}Bupy)I]$_2$	F 1.34 (75.1) G 2.01 (71.2)	I 4-^{t}Bupy	H 8.82 (6.6) (19.4) [d] I 7.09 (6.4) ^{t}Bu 1.32
[$PtMe_3$(4-Me_2Npy)$_2$I][1]	[$PtMe_3$(4-Me_2Npy)$_2$I]	A 1.35 (69.3) B 1.14 (71.5)	4-Me_2Npy I	H 8.29 (7.2) (19.6) [d] I 6.40 (7.2) NMe_2 3.02
	$PtMe_3$I	C 1.72 (77.3)	I	-
	anti-[$PtMe_3$(4-Me_2Npy)I]$_2$	D 1.27 (75.6) E 1.39 (70.0)	I 4-Me_2Npy	H 8.74 (7.1) (20.6) [d] I 6.49 (7.1) NMe_2 3.05
	syn-[$PtMe_3$(4-Me_2Npy)I]$_2$	F 1.27 (75.6) G 1.90 (70.1)	I 4-Me_2Npy	H 8.48 (7.0) (20.3) [d] I 6.20 (7.0) NMe_2 2.99

[a]Chemical shifts quoted in ppm are relative to an internal solvent peak ($CDCl_3$, δ 7.26 ppm). [b] $^2J_{Pt-H}$/Hz in parentheses. [c] $^3J_{H-H}$ /Hz in parentheses. [d] $^3J_{Pt-H}$ /Hz in parentheses. [e] labelling refers to scheme S1. Not all the scalar coupling resolved.

Table S2 Crystallographic data and structure refinement for mononuclear $[PtMe_3L_2I]$ complexes

Complex	**$[PtMe_3(4\text{-}NCpy)_2I]$**	**$[PtMe_3(4\text{-}Mepy)_2I]$**	**$[PtMe_3(4\text{-}Etpy)_2I]$**
CCDC No.	1037991	866046	823795
Empirical formula	$C_{15}H_{17}IN_4Pt$	$C_{15}H_{23}IN_2Pt$	$C_{17}H_{27}IN_2Pt$
Formula weight	575.32	553.34	581.39
T / K	123(2)	123(2)	133(2)
λ / Å	0.71073	0.71073	0.71073
Crystal color, shape	colorless, block	colorless, block	yellow, block
Crystal size/mm^3	0.300 x 0.200 x 0.100	0.380x0.140x0.140	0.410x0.210x0.180
Crystal system	Triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/n$	$P2_1/c$
a / Å	9.7124(5)	11.1252(4)	12.0156(17)
b / Å	10.2867(5)	12.8648(5)	12.0304(17)
c / Å	10.3892(5)	12.2536(3)	13.4566(19)
α / °	70.911(3)	90	90.00
β / °	66.286(3)	98.742(2)	102.370(3)
γ / °	73.069(3)	90	90.00
V / Å^3	882.64(8)	1733.40(10)	1900.0(5)
Z	2	4	4
$D_{calc.}$ (g cm^{-3})	2.165	2.120	2.032
μ / mm^{-1}	9.696	9.866	9.007
F(000)	532	1032	1096
θ / °	2.70 to 25.25	3.12 to 25.25	2.29 to 30.58
Completeness to θ_{full}	98.9 %	99.2%	99.9 %
Reflections collected	6324	10387	30865
Independent reflections	3174 [R(int) = 0.0243]	3119 [R(int) = 0.0281]	5833 [R(int) = 0.0201]
Absorption correction	multi-scan	multi-scan	multi-scan
Max. and min. trans.	0.7457, 0.4643	0.7457, 0.4865	0.433, 0.238
Data/restraints /parameters	3174/0/193	3119 / 0 / 177	5833/0/195
Goodness-of-fit on F^2	1.049	1.079	1.079
Final R indices [I> 2σ(I)]	R1 = 0.0215, wR2 = 0.0508	R1 = 0.0189, wR2 = 0.0398	R1 = 0.0146, wR2 = 0.0344
R indices (all data)	R1 = 0.0235, wR2 = 0.0514	R1 = 0.0220, wR2 = 0.0410	R1 = 0.0184, wR2 = 0.0359
Largest diff. peak and hole/ eÅ^{-3}	0.936, -1.136	0.589, -0.514	0.598, -1.298

Table S3 Crystallographic data and structure refinement for dinuclear $[PtMe_3LI]_2$ complexes

Complex	***syn*-$[PtMe_3(4\text{-}NCpy)I]_2$**	***anti*-$[PtMe_3(4\text{-}NCpy)I]_2$**	***syn*-$[PtMe_3(4\text{-}MeOpy)I]_2$**	***syn*-$[PtMe_3(4\text{-}Etpy)I]_2$**
CCDC No.	1037992	1037993	1037994	1037995
Empirical formula	$C_{18}H_{26}I_2N_4Pt_2$	$C_{18}H_{26}I_2N_4Pt_2$	$C_{18}H_{32}I_2N_2O_2Pt_2$	$C_{20}H_{36}I_2N_2Pt_2$
Formula weight	942.41	942.41	952.43	948.49
T / K	173(2)	173(2)	193(2)	193(2)
λ / Å	0.71073	0.71073	0.71073	0.71073
Crystal color, shape	pale-yellow, block	colorless, block	yellow, block	yellow, plate
Crystal size/mm^3	0.450x0.350x0.160	0.380x0.240x0.160	0.240x0.230x0.180	0.340x0.320x0.160
Crystal system	monoclinic	Monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	*P*nam
a / Å	8.88211(18)	8.0595(2)	10.4070(9)	10.7003(10)
b / Å	12.0880(2)	11.2505(3)	11.7649(6)	12.7871(9)
c / Å	22.6364(5)	13.6434(4)	20.7823(17)	18.4091(17)
α / °	90	90	90	90
β / °	99.0938(19)	106.090(3)	98.377(10)°	90
γ / °	90	90	90	90
V / Å ^{3}	2399.86(9)	1188.64(6)	2517.4(3)	2518.8(4)
Z	4	2	4	4
$D_{calc.}$ (g cm^{-3})	2.608	2.633	2.513	2.501
μ / mm^{-1}	14.228	14.363	13.568	13.554
F(000)	1696	848	1728	1728
θ / °	1.92 to 25.00	2.39 to 25.25	2.34 to 25.25	3.33 to 25.00
Completeness to θ_{full}	99.9 %	99.9 %	99.6 %	96.2%
Reflections collected	8366	4366	17067	16248
Independent reflections	4241 [R(int) = 0.0335]	2161 [R(int) = 0.0299]	4544 [R(int) = 0.0537]	2215 [R(int) = 0.0646]
Absorption correction	analytical	Gussian	multi-scan	multi-scan
Max. and min. trans.	0.344, 0.147	0.405, 0.159	0.1115, 0.0529	0.1480, 0.0562
Data/restraints /parameters	4241 / 0 / 241	2161 / 0 / 122	4544 / 0 / 245	2215 / 0 / 127
Goodness-of-fit on F^2	1.042	1.064	0.928	1.050
Final R indices [I> 2σ(I)]	R1 = 0.0302, wR2 = 0.0649	R1 = 0.0331, wR2 = 0.0868	R1 = 0.0232, wR2 = 0.0493	R1 = 0.0351, wR2 = 0.0925
R indices (all data)	R1 = 0.0339, wR2 = 0.0669	R1 = 0.0349, wR2 = 0.0887	R1 = 0.0334, wR2 = 0.0512	R1 = 0.0384, wR2 = 0.0947
Largest diff. peak and hole/ eÅ−3	1.431, -1.323	2.079, -1.932	0.844, -0.8777	2.340, -2.403

Table S4 Selected bond lengths (Å) and angles (°) in mononuclear $[PtMe_3L_2I]$ complexes (L = 4-NCpy, 4-Mepy, 4-Etpy)

Complex	$[PtMe_3(4\text{-}NCpy)_2I]$	$[PtMe_3(4\text{-}Mepy)_2I]$	$[PtMe_3(4\text{-}Etpy)_2I]$
Pt1-C1	2.053(4)	2.058(4)	2.053(2)
Pt1-C2	2.044(5)	2.055(4)	2.053(3)
Pt1-C3	2.077(4)	2.061(3)	2.069(3)
Pt1-N1	2.200(3)	2.176(3)	2.175(2)
Pt1-N2	2.185(4)	2.186(3)	2.189(2)
Pt1-I1	2.7784(3)	2.7723(3)	2.7771(4)
N1-Pt1-N2	88.57(12)	89.10(10)	90.67(6)
C1-Pt1-N1	178.77(16)	178.37(15)	176.89(9)
C2-Pt1-N2	177.02(15)	176.97(14)	178.58(9)
C3-Pt1-I3	177.99(14)	177.19(10)	178.11(7)

Table S5 Selected bond lengths (Å) and angles (°) in dinuclear $[PtMe_3LI]_2$ complexes

***anti*-$[PtMe_3(4\text{-}NCpy)I]_2$**			
Pt1-C1	2.047(9)	C1-Pt1-N1	178.9(3)
Pt1-C2	2.056(9)	C2-Pt1-I1	179.0(2)
Pt1-C3	2.057(9)	C3-Pt1-I1	177.2(3)
Pt1-N1	2.210(6)	Pt1-I1-Pt1a	92.46(2)
Pt1-I1	2.7956(6)	I1-Pt1-I1a	87.54(2)
***syn*-$[PtMe_3(4\text{-}NCpy)I]_2$**			
Pt1-C1	2.029(7)	C1-Pt1-N1	179.1(2)
Pt1-C2	2.045(7)	C2-Pt1-I2	178.3(2)
Pt1-C3	2.041(6)	C3-Pt1-I1	178.6(2)
Pt2-C4	2.043(7)	C4-Pt2-N4	177.5(2)
Pt2-C5	2.051(6)	C5-Pt2-I2	177.3(2)
Pt2-C6	2.043(7)	C6-Pt2-I1	179.6(2)
Pt1-N1	2.197(6)	Pt1-I1-Pt2	92.89(2)
Pt2-N2	2.210(6)	Pt1-I1-Pt2	93.06(2)
Pt1-I1	2.7916(5)	I1-Pt1-I2	86.67(2)
Pt1-I2	2.7927(5)	I1-Pt2-I2	86.89(2)
Pt2-I1	2.7908(5)		
Pt2-I2	2.7818(5)		
***syn*-$[PtMe_3(4\text{-}MeOpy)I]_2$**			
Pt1-C1	2.053(8)	C1-Pt1-N1	177.0(3)
Pt1-C2	2.054(8)	C2-Pt1-I1	179.6(3)
Pt1-C3	2.044(7)	C3-Pt1-I2	176.8(3)

Pt2-C4	2.047(9)	C4-Pt2-N2	177.2(3)
Pt2-C5	2.036(9)	C5-Pt2-I2	178.5(3)
Pt2-C6	2.029(8)	C6-Pt2-I1	177.7(3)
Pt1-N1	2.188(6)	Pt1-I1-Pt2	93.16(2)
Pt2-N2	2.181(6)	Pt1-I1-Pt2	92.64(2)
Pt1-I1	2.7839(5)	I1-Pt1-I2	86.92(2)
Pt1-I2	2.8116(5)	I1-Pt2-I2	86.82(2)
Pt2-I1	2.8020(5)		
Pt2-I2	2.7987(5)		
***syn*-[PtMe$_3$(4-Etpy)I]$_2$**			
Pt1-C1	2.054(8)	C1-Pt1-N1	178.3(3)
Pt1-C2	2.034(9)	C2-Pt1-I2	178.1(3)
Pt1-C3	2.061(9)	C3-Pt1-I1	178.4(2)
Pt1-N1	2.189(5)	Pt1-I1-Pt1a	92.00(2)
Pt1-I1	2.7785(6)	Pt1-I2-Pt1a	93.64(2)
Pt1-I2	2.8166(6)	I1-Pt1-I2	86.81(1)

References

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2. D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organomet. Chem.*, 1972, **38**, 403-420.