Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table S1. DFT calculated $\Delta\Delta G°_{f(complex)}$ values (kJ.mol^{-1}) for the stepwise ligand substitution reactions of $[PtX_{n-6}Y_n]^{2-}$ (n = 6 - 0)[a]

i	$[PtF_{n-6}Cl_n]^{2-}$ (n = 6 - 0)		$[PtF_{n-6}Br_n]^{2-}$ (n = 6 - 0)		$[PtCl_{n-6}I_n]^{2-}$ (n = 6 - 0)	
	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO
1	89.77	124.93	118.64	164.28	62.65	82.31
2	95.75	126.35	125.67	163.55	65.38	84.34
3	100.62	135.48	126.37	172.69	67.27	92.21
4	101.22	129.69	132.01	165.16	73.17	91.23
5	96.20	124.50	127.06	158.63	66.64	84.92
6	101.81	130.81	127.78	163.45	67.20	90.52
7	105.70	136.06	133.68	174.16	71.97	95.22
8	105.76	133.68	132.77	169.45	71.69	94.67
9	102.02	124.49	131.12	156.13	71.55	88.40
10	110.18	135.93	136.02	168.59	76.47	96.56

[a] - refer to Scheme S1 for i values (octahedral)

Table S2. DFT calculated and experimentally determined $\Delta\Delta G°_{f(complex)}$ values (kJ.mol^{-1}) for the stepwise ligand substitution reactions of $[PtCl_{n-6}Br_n]^{2-}$ (n = 6 - 0)

i	PBE		LDA		PW91		M06L		Experimental
	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO	
1	23.61	31.40	24.40	31.02	23.63	31.33	35.93	45.15	18.51
2	25.48	32.77	27.68	34.67	27.15	34.65	41.76	50.36	21.13
3	27.04	37.31	29.43	37.49	28.81	37.13	42.94	53.92	23.47
4	29.12	36.66	30.51	37.41	30.16	37.25	44.39	49.97	23.22
5	25.63	30.69	25.79	32.47	25.42	32.74	40.53	48.09	19.5
6	27.24	34.75	26.64	34.52	26.21	33.96	40.74	51.83	20.86
7	28.66	36.07	31.32	39.47	30.84	38.02	48.18	59.53	24.86
8	27.34	34.48	29.75	37.45	29.37	36.27	45.67	56.36	22.71
9	27.84	34.60	28.03	34.63	27.82	34.25	40.91	46.97	20.09
10	30.96	42.22	33.05	40.17	32.16	39.77	56.33	64.20	25.42

Table S3. DFT calculated and experimentally determined $\Delta G°_{rxn}$ values (kJ.mol^{-1}) for the isomerisation reactions of $[PtCl_{n-6}Br_n]^{2-}$ (n = 6 - 0)

i	PBE		LDA		PW91		M06L		
	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO	Experimental
11	-1.56	-4.54	-1.75	-2.82	-1.66	-2.47	-1.18	-3.56	-2.35
12	-1.93	-1.44	-2.97	-2.13	-3.08	-2.04	-2.68	1.68	-1.38
13	0.51	0.12	-1.72	-2.82	-1.55	-2.02	-4.76	-9.38	-2.62

Table S4. DFT calculated and experimentally determined $\Delta\Delta G°_{f(complex)}$ values (kJ.mol^{-1}) for the 'cross' ligand substitution reactions of $[PtCl_{n-6}Br_n]^{2-}$ (n = 6 - 0)

i	PBE		LDA		PW91		M06L		
	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO	Gas phase	COSMO	Experimental
14	27.56	32.13	28.76	34.59	28.50	34.77	43.21	46.41	25.56
15	27.19	35.23	27.54	35.28	27.08	35.21	41.71	51.65	24.59
16	26.73	34.63	28.35	37.34	27.76	35.99	45.50	61.22	23.48
17	29.16	36.19	29.60	36.65	29.29	36.00	43.42	50.15	22.31

Gaussian 09 COMPUTATIONAL DETAILS

Geometries were fully optimised at the DFT (LSDA, PBEVWN, M06L, B3LYP, PBE1PBE, M06, CAM-B3LYP and HSEH1PBE) and MP2 levels of theory using the LanL2DZ basis set in both the gas phase as well as for those using Polarizable Continuum Model (PCM), with the parameters of water. The obtained structures were characterized as minima by analyzing the Hessian matrix. These calculations employed the Gaussian 09, Revision B.01 program.[1]

Gaussian 09, Revision B.01,

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.