

A combined kinetic-mechanistic and computational study on the competitive formation of seven- *versus* five-membered platinacycles; the relevance of spectator halide ligands

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Supporting Information

Table S1.- Values of k_{obs} for all the systems studied in xylene solution as a function of temperature and pressure, $[\text{Pt}] = (0.5\text{-}5.0)\times 10^{-4}$ M.

System	$T / ^\circ\text{C}$	P / atm	$k_{\text{obs}} / \text{s}^{-1}$
5-IV-Br,F \rightleftharpoons II-Br,F	60	1	$2.3 \square 10^{-5}$
	60	400	$2.7 \square 10^{-5}$
	60	700	$2.8 \square 10^{-5}$
	60	950	$3.8 \square 10^{-5}$
	60	1200	$5.5 \square 10^{-5}$
	60	1500	$6.5 \square 10^{-5}$
	70	1	$9.8 \square 10^{-5}$
	80	1	$36 \square 10^{-5}$
	90	1	$93 \square 10^{-5}$
II-Br,F \rightleftharpoons II'-Br,F	55	400	$2.3 \square 10^{-5}$
	55	700	$2.5 \square 10^{-5}$
	55	950	$2.5 \square 10^{-5}$
	55	1200	$3.2 \square 10^{-5}$
	55	1500	$3.1 \square 10^{-5}$
	60	1	$4.6 \square 10^{-5}$
	70	1	$7.8 \square 10^{-5}$
	80	1	$13 \square 10^{-5}$
	90	1	$20 \square 10^{-5}$
5-IV-Cl,F \rightleftharpoons II-Cl,F	60	1	0.0015
	70	1	0.0059
	80	1	0.0075
	89	1	0.012
II-Cl,F \rightleftharpoons II'-Cl,F	60	1	$3.7 \square 10^{-5}$
	70	1	$7.8 \square 10^{-5}$
	80	1	$18 \square 10^{-5}$
	89	1	$87 \square 10^{-5}$
II-Cl,F \rightleftharpoons 7-II-Cl,F	70	1	$2.3 \square 10^{-5}$
	80	1	$4.1 \square 10^{-5}$
	89	1	$7.7 \square 10^{-5}$

Table S2.- Computed relative free energy values (in kJ mol^{-1}) for the formation of **7-II-X,F** from **II'-X,F** according to Scheme 6, bottom .

Step/X	Br	Cl
II'-X,F	0.0	0.0
II'a-X,F	89.3	90.8
TS_CH2	138.1	137.1
II'c-X,F	121.5	119.5
TS_RE2	137.5	136.4
7-II-X,F	-44.4	-44.9

Table S3.- Computed B3LYP electronic energy (E_{el}) with the large basis sets (6-311+G**/aug-cc-pVTZ), thermal correction to the enthalpy (H_{corr}) and entropic term ($T\Delta S$), and free energy values (in Hartrees) in xylene for all the species at 139°C. H_{corr} contains the zero-point energy, the vibrational, rotational and translational energies as well as the thermal correction (RT). The final free energies are obtained with the formula: $\Delta G_{139^\circ C} = E_{el} + H_{corr} - T\Delta S$

Species	E_{el}	H_{corr}	TDS	$\Delta G_{139^\circ C}$
II-Br,H (E)	-1616.53152	0.5171	0.1317	-1616.14607
II-Br,H (Z)	-1616.53207	0.5174	0.1309	-1616.14562
Ila-Br,H	-1616.48907	0.5152	0.1352	-1616.10909
TS_Isom-Br,H	-1616.46936	0.5146	0.1385	-1616.09334
II'a-Br,H	-1616.50038	0.5164	0.1338	-1616.11777
II'-Br,H (E)	-1616.53978	0.5171	0.1294	-1616.15209
II'-Br,H (Z)	-1616.53747	0.5174	0.1292	-1616.14923
TS_CH1-Br,H	-1616.48343	0.5113	0.1344	-1616.10653
II'b-Br,H	-1616.48584	0.5130	0.1351	-1616.10796
TS_RE1-Br,H	-1616.47586	0.5115	0.1338	-1616.09820
5-II-Br,H	-1344.88474	0.3792	0.1032	-1344.60871
TS_CH2-Br,H	-1616.47531	0.5110	0.1320	-1616.09633
II'c-Br,H	-1616.48478	0.5115	0.1306	-1616.10395
TS_RE2-Br,H	-1616.47835	0.5111	0.1296	-1616.09684
7-II-Br,H	-1344.87498	0.3795	0.1011	-1344.59659
II'-Br,F (E)	-1715.80537	0.5096	0.1227	-1715.41854
II'a-Br,F	-1715.76639	0.5089	0.1270	-1715.38452
TS_CH2-Br,F	-1715.74347	0.5036	0.1259	-1715.36594
II'c-Br,F	-1715.75294	0.5051	0.1243	-1715.37227
TS_RE2-Br,F	-1715.74581	0.5036	0.1239	-1715.36615
7-II-Br,F	-1444.14350	0.3722	0.0969	-1443.86834
II-Cl,H (E)	-1659.83421	0.5175	0.1269	-1659.44366
II-Cl,H (Z)	-1659.83487	0.5178	0.1263	-1659.44338
Ila-Cl,H	-1659.79008	0.5153	0.1338	-1659.40858
TS_Isom-Cl,H	-1659.77009	0.5147	0.1349	-1659.39031
II'a-Cl,H	-1659.80339	0.5166	0.1319	-1659.41869
II'-Cl,H (E)	-1659.84347	0.5172	0.1297	-1659.45596
II'-Cl,H (Z)	-1659.84104	0.5177	0.1280	-1659.45136
TS_CH1-Cl,H	-1659.78721	0.5115	0.1314	-1659.40705
II'b-Cl,H	-1659.78928	0.5131	0.1311	-1659.40726
TS_RE1-Cl,H	-1659.77809	0.5116	0.1302	-1659.39671
5-II-Cl,H	-1388.18827	0.3793	0.1014	-1387.91035
TS_CH2-Cl,H	-1659.77982	0.5113	0.1303	-1659.39891
II'c-Cl,H	-1659.78923	0.5115	0.1264	-1659.40417
TS_RE2-Cl,H	-1659.78270	0.5113	0.1277	-1659.39916
7-II-Cl,H	-1388.17891	0.3799	0.0987	-1387.89763
II'-Cl,F (E)	-1759.10887	0.5097	0.1210	-1758.72028
II'a-Cl,F	-1759.06950	0.5091	0.1252	-1758.68570
TS_CH2-Cl,F	-1759.04684	0.5037	0.1248	-1758.66807
II'c-Cl,F	-1759.05748	0.5053	0.1225	-1758.67478
TS_RE2-Cl,F	-1759.05011	0.5038	0.1219	-1758.66833
7-II-Cl,F	-1487.44730	0.3724	0.0953	-1487.17029
Toluene	-271.65490	0.1359	0.0512	-271.57017

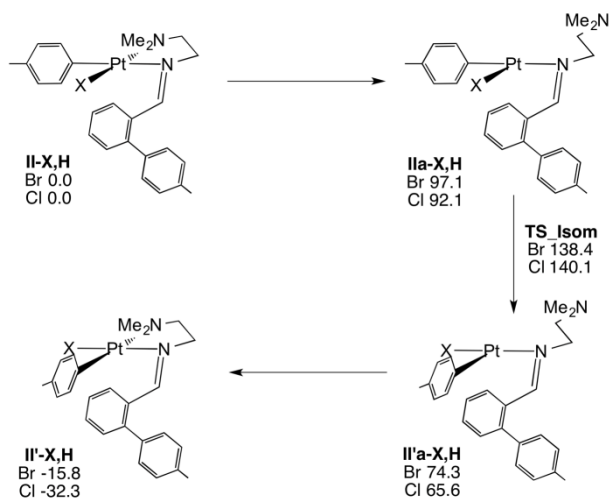


Figure S1.- Isomerization process transforming II-X,H into II'-X,H (free energies in kJ mol^{-1}).

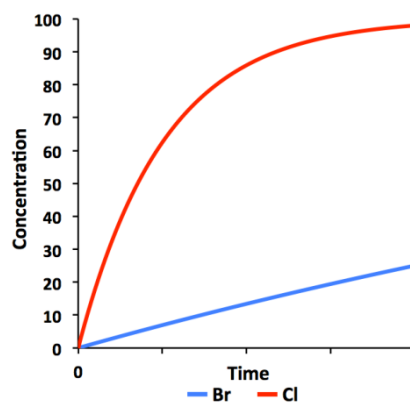


Figure S2.- Qualitative product concentration II'-X,F vs 7-II-X,F evolution over time for ($X = \text{Br, Cl}$) in arbitrary time scale.