

**Kinetico-mechanistic studies on the formation of seven-membered
[C,N]-platinacycles: the effect of methyl or fluoro substituents on the
aryl ancillary ligands**

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

Starting material	$T/^{\circ}\text{C}$	P/atm	fast $k_{\text{obs}}/\text{s}^{-1}$	slow $k_{\text{obs}}/\text{s}^{-1}$
5₁-MeBrF	30	1	4.0×10^{-4}	0.60×10^{-4}
	40	1	10×10^{-4}	1.5×10^{-4}
		600	11×10^{-4}	1.3×10^{-4}
		900	8.5×10^{-4}	1.3×10^{-4}
		1200	8.3×10^{-4}	1.3×10^{-4}
		1500	7.4×10^{-4}	1.5×10^{-4}
		1800	9.1×10^{-4}	1.4×10^{-4}
	50	1	28×10^{-4}	3.2×10^{-4}
5₁-FBrF	60	1	53×10^{-4}	6.6×10^{-4}
	40	1	1.1×10^{-4}	0.15×10^{-4}
	50	1	4.6×10^{-4}	0.52×10^{-4}
		300	5.3×10^{-4}	not determined
		400	4.5×10^{-4}	0.69×10^{-4}
		600	3.8×10^{-4}	0.77×10^{-4}
		900	4.2×10^{-4}	0.77×10^{-4}
		1200	3.5×10^{-4}	1.5×10^{-4}
		1500	3.9×10^{-4}	1.6×10^{-4}
	60	1	13×10^{-4}	1.4×10^{-4}
	70	1	26×10^{-4}	2.4×10^{-4}
	80	1	60×10^{-4}	7.6×10^{-4}
5₂-HBrF	40	1	4.0×10^{-4}	
	45	700	32×10^{-4}	
		1000	24×10^{-4}	
		1300	18×10^{-4}	
		1600	12×10^{-4}	
		1900	8.0×10^{-4}	
	50	1	16×10^{-4}	
	60	1	44×10^{-4}	
5₂-MeBrH	30	1	3.6×10^{-4}	0.49×10^{-4}
		400	3.6×10^{-4}	not determined
		700	3.5×10^{-4}	not determined
		1000	2.8×10^{-4}	not determined
		1300	2.6×10^{-4}	not determined
		1600	2.5×10^{-4}	not determined
	40	1	8.7×10^{-4}	1.5×10^{-4}
	50	1	19×10^{-4}	8.7×10^{-4}
	54	400	not determined	6.0×10^{-4}
		700	not determined	5.4×10^{-4}
		1000	not determined	5.2×10^{-4}
		1300	not determined	5.8×10^{-4}
		1600	not determined	5.6×10^{-4}
	60	1	50×10^{-4}	8.0×10^{-4}
	30	1	4.1×10^{-4}	0.15×10^{-4}
	35	400	5.7×10^{-4}	
5₂-MeBrH		700	4.6×10^{-4}	
		1000	3.8×10^{-4}	
		1300	3.0×10^{-4}	
		1600	2.7×10^{-4}	
	40	1	6.8×10^{-4}	0.45×10^{-4}
	50	1	13×10^{-4}	0.96×10^{-4}
	60	1	27×10^{-4}	3.5×10^{-4}
	62	700	not determined	4.7×10^{-4}
		1000	not determined	4.8×10^{-4}
		1300	not determined	4.8×10^{-4}
		1600	not determined	5.0×10^{-4}
		1800	not determined	4.9×10^{-4}

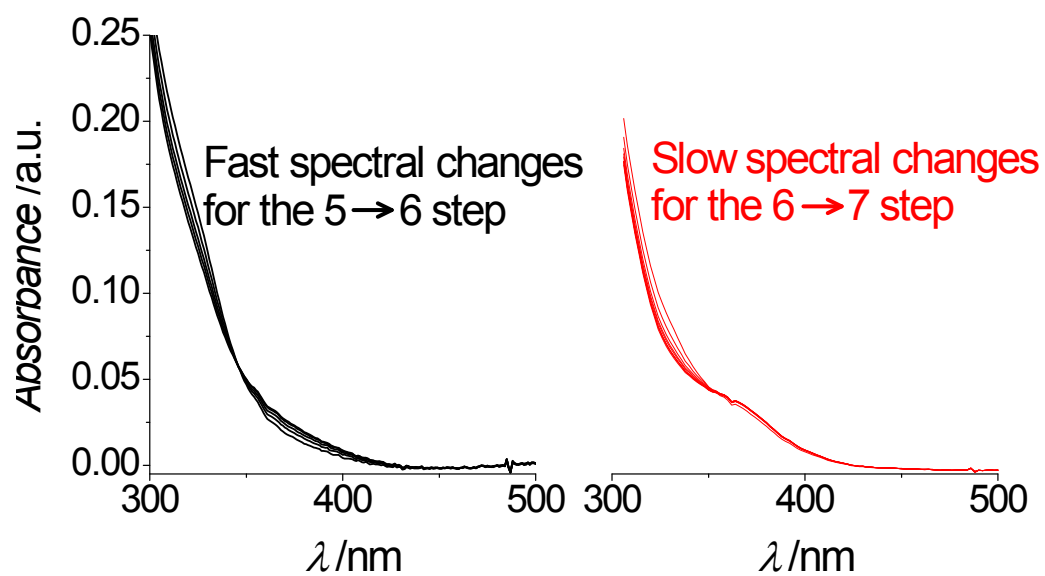


Figure S1.- Two step UV-Vis spectral changes observed on a 5×10^{-4} M toluene solution of **5I-MeBrF**, (30 °C 6 hours for the fast ~~5 $\times$ 6~~ step, 50 °C 3.5 hours for the slow ~~6 $\times$ 7~~ step).