ISOMERIZATION ON SUBSTITUTION PROCESSES ON CYCLOMETALLATED DIMETHYLHALOPLATINUM(IV) COMPLEXES.

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Supporting information: 7 pages

Table S1.- Values of k_{obs} determined as a function of platinum compound, temperature, and entering and leaving ligand concentrations.

FIGURE S1.- Plot of the absolute intensity of the ^{ax}Me central signal of compound **1** during the substitution process by PPh_3 at 260 K in chloroform solution.

FIGURE S2.- Room temperature proton NMR partial spectrum of compound **3**, $CDCl_3$, 200 MHz. ***a***) indicates the signals corresponding to the SMe_2 of the *fac***3** isomer; ***b***) indicates the signals corresponding to the SMe_2 of the *mer***3** isomer

FIGURE S3.- Temperature evolution of the proton NMR signals of the SMe_2 of the *fac***5**/*mer***5** mixture of isomers, $CDCl_3$, 500 MHz. ***a***) indicates the signals corresponding to the platinum satellites of the *fac* isomer; ***b***) indicates the signals corresponding to the *mer* isomer; ***c***) indicates the uncoupled signal of the *fac* isomer plus that of free sulfide.

Table S1.– Values of k_{obs} determined as a function of platinum compound, temperature, and entering and leaving ligand concentrations.

Compound	T /°C	P /atm	$10^3\times$[PPh_3] /M	$10^3\times$[SMe_2] /M	$10^3\times k_{obs}$ /s^{-1} Fast	Slow
*mer***3**	10	1	3.0	7.5	5.7	–
			5.0	5.0	13	–
			5.0	53	1.4	–
			6.0	33	2.6	–
			8.0	63	2.0	–
			25	2.5	52	2.1
	15	1	10	2.5	–	5.5
			20	2.5	–	5.4
	20	1	2.5	2.5	59	13
			2.5	5.0	48	–
			2.5	7.5	26	–
			2.5	10	21	–
			2.5	15	14	–
			5.0	2.5	129	10
			7.5	2.5	185	11
			10	2.5	170	12
			10	2.5	–	11
			10	5.0	–	12
			10	15	44	–
			10	15	48	–
			13	2.5	180	12
			15	2.5	200	13
			18	2.5	200	12
			20	2.5	–	12
			20	5.0	–	12
			23	2.5	200	11
			30	2.5	240	11
	30	1	3.0	7.5	56	–
			5.0	5.0	150	41
			5.0	53	15	–
			6.0	33	29	–
			8.0	63	20	–
			10	2.5	–	43
			10	5.0	–	43
			20	2.5	–	42
			20	5.0	–	45

			25	2.5	620	46
		300	20	2.5	–	44
		600	20	2.5	–	38
		900	20	2.5	–	31
		1200	20	2.5	–	26
		1500	20	2.5	–	22
		1800	20	2.5	–	18
	35	1	10	2.5	–	100
			20	2.5	–	110
	40	1	3.0	7.5	350	–
			5.0	5.0	780	200
			5.0	53	68	–
			6.0	33	170	–
			8.0	63	85	–
			25	2.5	2900	240
*mer***4**	10	1	3.0	7.5	3.3	–
			5.0	5.0	5.5	0.87
			5.0	53	0.87	–
			6.0	33	1.6	–
			8.0	63	1.1	–
			25	2.5	12	0.89
	20	1	3.0	7.5	13	–
			5.0	5.0	27	3.9
			5.0	53	4.8	–
			6.0	33	10	–
			8.0	63	6.7	–
			25	2.5	67	4.3
		300	20	2.5	–	2.6
		600	20	2.5	–	2.0
		900	20	2.5	–	1.5
		1500	20	2.5	–	0.93
		1800	20	2.5	–	0.75
	30	1	3.0	7.5	64	–
			5.0	2.5	120	15
			5.0	5.0	95	16
			5.0	53	28	–
			6.0	33	44	–
			10	2.5	140	17
			13	53	53	–
			25	2.5	170	18
	40	1	5.0	5.0	–	51
			25	2.5	–	59

*mer***5**	9.0	1	20	–	230	–
	20	1	3.0	7.5	280	–
			5.0	5.0	480	–
			5.0	53	80	–
			6.0	33	120	–
			8.0	63	91	–
			25	2.5	1000	–
	30	1	20	–	2800	–
	40	1	20	–	7400	–

FIGURE S1

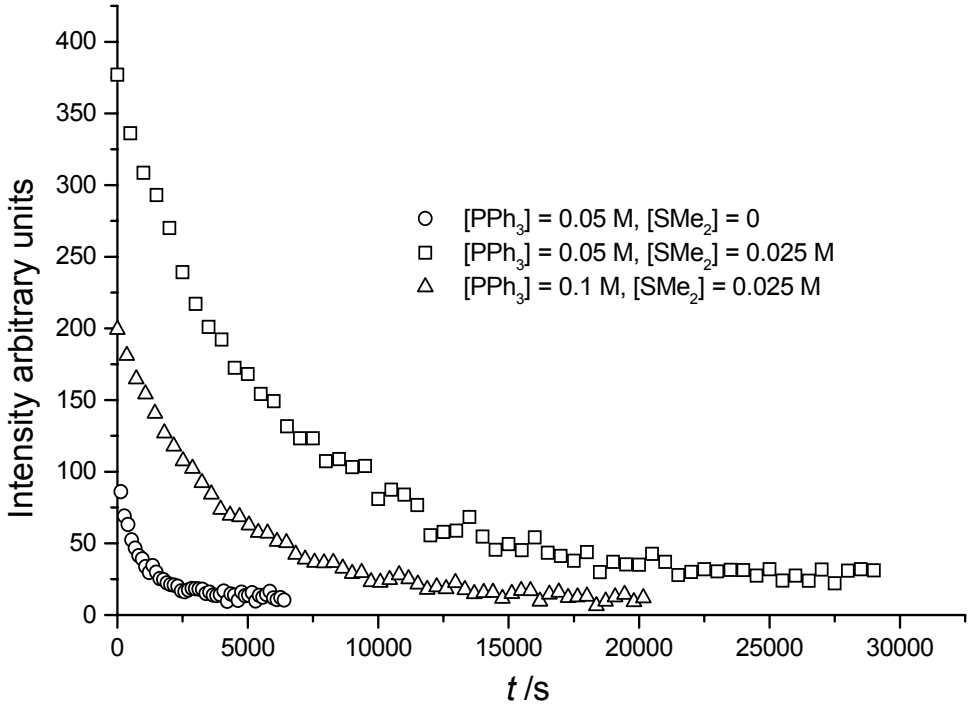
Intensity arbitrary units
400
350
300
250
200
150
100
50
0
0
5000
10000
15000
20000
25000
30000
t /s
[PPh3] = 0.05 M, [SMe2] = 0
[PPh3] = 0.05 M, [SMe2] = 0.025 M
[PPh3] = 0.1 M, [SMe2] = 0.025 M

FIGURE S2

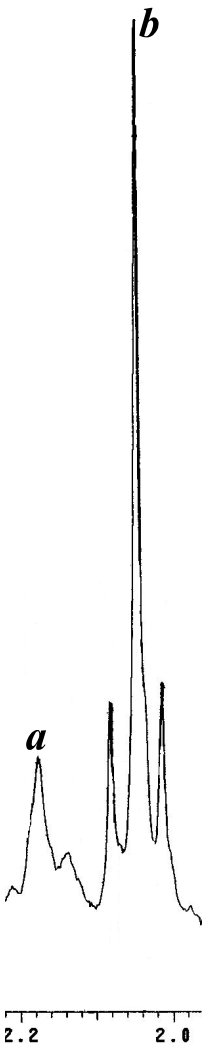

FIGURE S3