Kinetico–mechanistic studies of C–H bond activation on new Pd complexes containing N,N' chelating ligands

Isabelle Favier,[a] Montserrat Gómez,[a] Jaume Granell,[a] Manuel Martínez,[a] Xavier Solans,[b] and Mercè Font–Bardía[b]

[a] Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1–11, E–08028 Barcelona, SPAIN.

[b] Departament de Mineralogia, Cristal·lografia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, E–08028 Barcelona, SPAIN.

Table S1.- Values of k_{obs} for the systems studied, as a function of the starting coordination compound, temperature and pressure, in neat acetic acid unless stated; [Pd] = (5–10)×10^{-4} M. All the values are the average of 2 to 4 runs.

Palladium complex	T /ºC	P /atm	$10^4 \times k_{obs}$ /s^{-1}
E–**1AcO**	26	1	0.41
	30	1	0.43
	44	1	2.8
	51	400	13
	51	500	15
	51	600	16
	51	800	17
	51	1100	20
	51	1400	21
	52	1	9.0
	59	1	14
	62	1	28
	69	1	38
E–**1Cl**	30	1	0.35
	41	1	0.89
	56	1	4.9
	55	400	5.0
	55	500	5.5
	55	700	5.6
	55	1000	6.1
	55	1300	6.9
	55	1600	8.2
	68	1	15
Z–**1AcO**	50	1	0.080
	60	1	0.25
	70	1	0.73
	75	400	1.3
	75	700	1.8
	75	1000	1.2
	75	1300	1.1

	75	1600	1.5
	80	1	2.4
Z–**1Cl**	55	1	0.066
	70	1	0.35
	88	1	1.6
E–**2AcO(M)**[a]	26	1	0.25
	29	1	0.23
	30	1	0.43
	30	1	0.25
	40	1	1.3
	44	1	2.8
	50	1	4.3
	50	400	7.9
	50	600	9.5
	50	750	9.9
	50	800	12
	50	1100	13
	50	1250	14
	50	1400	18
	50	1500	20
	52	1	9.0
	59	1	20
	60	1	13
	62	1	28
	65	1	31
	69	1	54
E–**2AcO(m)**[b]	20	1	7.0
	30	1	17
	49	1	35
E–**2Cl(M)**	30	1	0.18
	32	1	0.38
	35	1	0.47
	40	1	0.49
	45	1	1.3
	50	1	3.0
	55	1	4.6

	56	400	10
	56	700	12
	56	1000	16
	56	1300	17
	56	1600	19
	60	1	6.1
	64	1	9.0
	69	1	14
E–**2Cl(m)**[b]	18	1	17
	20	1	21
	30	1	39
	40	1	60

[a] The same values were obtained, within experimental error, from the measures from the crude *E*–**2AcO(M)**+*E*–**2AcO(m)** (4/1) mixture obtained in the preparation of the *E*–**2AcO** complex (see text).

[b] Measured as the fast reaction by the addition of 0.05 cm^3 of a concentrated solution of the crude palladium complex mixture of *E*–**2AcO** and *E*–**2Cl** in CH_2Cl_2 to 2.5 cm^3 of neat acetic acid.

Table S2.- Values of k_{obs} for the systems studied, as a function of the starting coordination compound, temperature and acetic acid concentration, in toluene solution, or triflic acid in acetic acid solution; $[Pd] = (5-10)\times10^{-4}$ M. All the values are the average of 2 to 4 runs.

Palladium complex	T /°C	$[CH_3CO_2H]$ /M	$10^3\times[HTrif]$ / M	$10^4\times k_{obs}$ /s^{-1}
E-**1AcO**	31	16	–	0.51
	31	16	1.3	14
	31	16	3.8	6.4
	31	16	6.4	4.4
E-**1Cl**	30	16	–	0.35
	30	16	1.3	51
	30	16	3.8	42
	30	16	6.4	36
	30	16	10	25
	30	16	13	23
E-**2AcO(M)**	29	16	-	0.23
	29	12	-	0.15
	29	8.5	-	0.10
	29	5.7	-	0.12
	40	16	-	1.3
	40	16	1.5	23
	40	16	3.0	13
	40	16	6.1	8.2
	40	16	9.1	6.1
	40	16	12	5.2
	40	13	-	0.85
	40	11	-	0.73
	40	8.0	-	0.61
	40	5.1	-	0.44
	40	2.9	-	0.38
	50	16	-	4.3
	50	14	-	2.9
	50	13	-	2.1
	50	11	-	1.6
	50	8.6	-	1.4

60	16	-	11
60	11	-	5.7
60	8.6	-	4.9
60	5.7	-	3.5
60	2.9	-	2.3

FIGURE S1.– Variation of the value of k_{obs} with the concentration of acid in solutions of complex *E–**2AcO(M)*** in acetic acid/toluene mixtures at different temperatures (▲, 40 °C; ■, 60 °C).
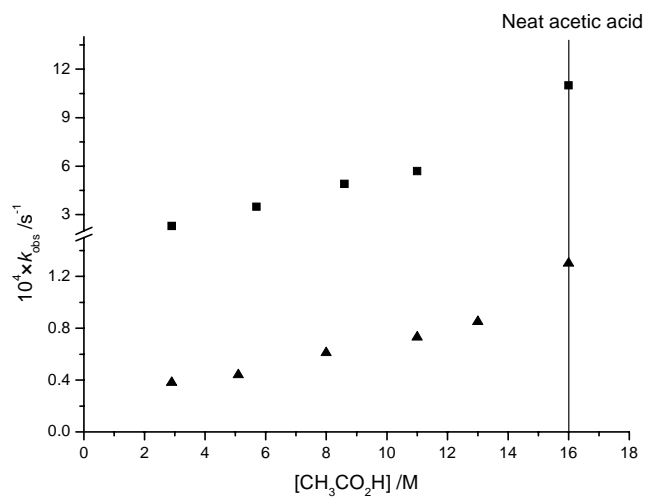
FIGURE S2.– Variation of the value of k_{obs} for the cyclometallation reaction of *E–**2AcO(M)*** with the concentration of triflic acid in neat acetic acid at 40 °C.
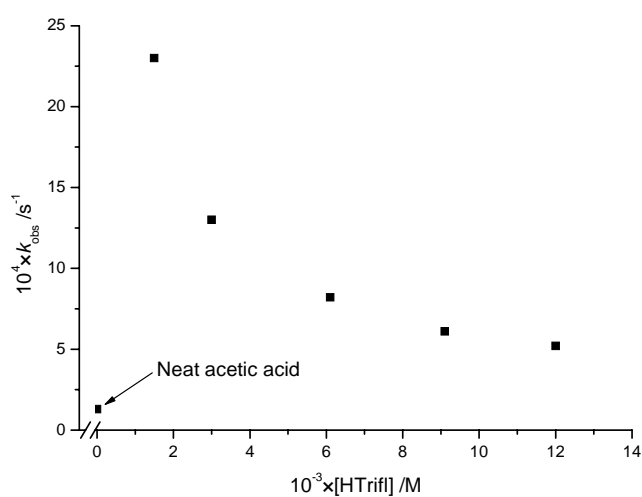
FIGURE S3.– Eyring plot for the variation of the rate constants for the cyclometallation reaction of compounds *E*–**1AcO** (▲), *E*–**2AcO(m)** (◆) and *E*–**2Cl(M)** (●) in acetic acid solution.